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SERIES A
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VOL. LXXVI.

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PROCEEDINGS OF THE ROYAL SOCIETY.

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*Address delivered by the President, Sir William Huggins,
K.C.B., O.M., F.R.S., at the Anniversary Meeting on
November 30th, 1904.*

Since the last Anniversary the Society has lost by death fourteen Fellows.
The deceased Fellows are :—

Sir Frederick Bramwell, born 1818, died Nov. 30, 1903.

Robert Etheridge, born Dec. 3, 1819, died Dec. 18, 1903.

George Salmon, born Sept. 25, 1819, died Jan. 22, 1904.

Lieut.-General C. A. McMahon, born March 23, 1830, died Feb. 21,
1904.

Sir C. Le Neve Foster, born Mar. 23, 1841, died April 19, 1904.

George Johnston Allman, born 1824, died May 8, 1904.

Alexander William Williamson, born May 7, 1824, died May 6, 1904.

Robert McLachlan, born April 10, 1837, died May 23, 1904.

Isaac Roberts, born 1829, died July 17, 1904.

Sir John Simon, born Oct. 10, 1816, died July 23, 1904.

Joseph David Everett, born 1831, died Aug. 9, 1904.

Sir William Vernon Harcourt, born Oct. 14, 1827, died Oct. 1, 1904.

Frank McClean, born 1837, died Nov. 8, 1904.

Earl of Northbrook, born 1826, died Nov. 15, 1904.

Memorial Notices of the Fellows who have been taken from us by death
during the past year will appear in due course in the Obituary Notices.

Of some of them only, on this occasion, will time permit me to give expression, on your behalf, to a few words of appreciation of their work, and of deep sorrow at their loss.

In your name I place a wreath, emblem of our respect and of our deep sorrow, to the memory of our late Fellow and Copley-Medallist, the revered Provost of Trinity College, Dublin, who passed away at the ripe age of eighty-four years. George Salmon was as remarkable in the influence of his powerful personality, as in his works, by which he extended and adorned two domains of thought, as diverse as mathematics and theology. It is given to few men to achieve a European reputation as an investigator of the first rank in two distinct provinces of knowledge.

Born and educated in the City of Cork, he matriculated at Trinity College, Dublin, at the early age of fourteen. After a brilliant undergraduate course, he took his degree in 1838, and was elected a Fellow in 1841. Devoting himself to the study of pure mathematics, he produced a series of books, now accounted as classics in every university of the world, which were of very great service in promoting the advancement of that science. Their value was shown by the number of their editions, by their translation into several languages, and by the honours they procured for their author. In his "Lessons Introductory to the Study of the Modern Higher Algebra," which grew in subsequent editions until it became a treatise, he made accessible to the student the recent researches of the previous twenty years into the theory of transformations of binary forms.

Following the traditions of the Dublin School of Mathematics, he gave wide scope in all his books to geometrical method, often relieving the monotony of pages of analysis by the introduction of a brilliant geometrical proof.

In 1866, on the preferment of Dr. Butcher, Salmon was appointed Regius Professor of Divinity, from which time he ceased to work at mathematics, except in an occasional way at the Theory of Numbers. This is not the place for a consideration of his contributions to theological literature, nor of his great influence in the Church in Ireland at a time of exceptional difficulty. One important aspect of his theological labours is expressed by the title which was given to him of "*malleus Germanorum*."

In the year 1888 he was appointed by the Lord Lieutenant to the post of Provost of Trinity College. His large sympathy with all sorts and conditions of men, his unaffected dignity, his genial humour, and his kind heart, gave to his masterful tenure of the office of Provost an influence probably unparalleled in the history of Trinity College.

Not Trinity College alone, but all Dublin was proud of him. Men of all

classes and creeds praised him. His private tastes were simple ; his chief relaxations, chess playing, music, and novel reading. In the words of the late Bishop of Oxford :—"The Provost is an extraordinary man. The first day I met him I was most struck by his gracious courtesy, the second day by his learning, the third day by his humour, and every day by his humility."

The Fates are inexorable ; there may be long delay, but always at last the thread is cut. In midsummer our oldest Fellow, in point of election as well as of age, passed from us :—Sir John Simon, the pioneer of modern sanitary science. What Lister did for surgery, and Pasteur for bacteriology, Simon may be said to have accomplished for sanitation. Very early he perceived clearly and developed the true nature and mode of dealing with contagious emanations proceeding from the sick, establishing a doctrine and practice which afterwards received their direct proof and further development in the growth of the new science of bacteriology. Deeply grateful to his memory, we mourn one who by his life-work conferred incalculable benefit upon the whole civilized world.

Simon commenced the study of medicine in 1833, and attended both St. Thomas's Hospital and the recently established King's College. It was in 1848 that his attention was definitely directed to that branch of the profession with which his name will always remain famous, and which indeed he may almost be said to have founded, through his election to the newly-constituted post of Medical Officer of Health to the City of London. Seven years later a Central Board of Health was created, on which Simon represented medicine. When the functions of the Board were transferred to the Privy Council, he became adviser to the Government on all sanitary and medical matters. It is not possible on this occasion to indicate, even broadly, his strenuous work through a long life for the public good. His writings consist mainly of his numerous official reports, together with a volume published in 1857, entitled "Papers on the History and Practice of Vaccination," followed in the next year by a "Report on the Sanitary State of the People of England," which brought out for the first time the wide variations which exist in the local incidence of diseases. His great work on "English Sanitary Institutions" appeared in 1890. In 1878 he was elected President of the Royal College of Surgeons ; he was the recipient of numerous honours from scientific bodies at home and abroad. At the Jubilee in 1887 he received from Queen Victoria the distinction of K.C.B. These public recognitions were the outward signs of the universal respect and honour accorded him by all men. His memory will ever remain green in the history of sanitary science.

In May passed away, full of years and full of honours, a Fellow to whose personal services the Society is largely indebted—Professor Williamson. Elected into the Society in 1855, after serving twice upon the Council, he became Foreign Secretary in 1873, which office he held for sixteen years, until 1889. Half a century ago Williamson took a prominent part in the development of chemical thought, and exercised a powerful influence on chemical teaching in this country. He began the study of chemistry at Heidelberg, but soon passed to Liebig's laboratory at Giessen, where he took his degree, and while there published papers on the decomposition of Oxides and Salts by Chlorine, and on "The Blue Compounds of Cyanogen and Iron." He then went to Paris, where he came under the teaching of Comte. In 1849 he left Paris to occupy the chair of practical chemistry in University College, from which he continued to teach for thirty-eight years. A little later he published the classical research, elucidating the process of the formation of ether, with which his name will always remain associated. This paper, a model of concise reasoning founded upon happily devised experiment, produced a profound influence on contemporary thought, and received the assent of the whole chemical world. In this paper he gave his acceptance of the doctrine of types, which was prominent in his subsequent teaching. Williamson was a pioneer of chemical thought in quite another direction by the introduction of the conception of dynamics into chemical processes. He advanced the view, which is fundamental in the modern hypothesis of ionic dissociation, that in substances which appear at rest, the atoms of the molecules of the compound are in motion, exchanging from one molecule to another in an unending course of ionic migrations.

Williamson occupied the chair of the British Association in 1873, and was twice President of the Chemical Society. Honorary degrees were conferred upon him by the Universities of Dublin, Edinburgh, and Durham, and he received the honorary membership of many scientific societies. Seventeen years ago he retired from professional life to Hindhead.

Alas! this room will know no more a frequent and welcome attendant at our meetings who often took part in our discussions. A man whose great natural vitality and intellectual activity were so remarkable and unimpaired, that his sudden death came as a great shock to his many friends. Professor Everett was born and educated at Ipswich, and after graduating with honours at Glasgow, he became Professor of Mathematics at King's College, Nova Scotia. Later, in 1867, he was appointed Professor of Natural Philosophy at Queen's College, Belfast, a chair which he occupied with distinction for thirty years. Since his retirement, about seven years ago, he has resided in London,

taking an active part in the proceedings of scientific societies, especially of the Physical Society, of which he was a Vice-President. Professor Everett rendered important service to physical science, by his admirable translation of Deschanel's "Treatise of Natural Philosophy," which he brought up to date from time to time by the necessary additions and alterations, and by his "Illustrations of the C.G.S. System," which was translated into several languages, and proved of material service in the establishment of a physical system of units. He did important work as the secretary of the Committee of the British Association which effected the selection and naming of these dynamical and electrical units, and also of the Committee which has collected our main knowledge of underground temperatures. He was the inventor of a system of shorthand, which provides greater facilities for vowel insertion than other systems. He was enthusiastically devoted to cycling. A man of great kindness and geniality, he is regretted by a large circle of friends, and will always be remembered by his numerous pupils with much gratitude and affection.

Death has deprived us of a Fellow whose genial humour, clear judgment, and ready wit endeared him to many friends—Sir Frederick Bramwell. In Bramwell the love of things mechanical was inborn. At the time of his youth, technical education was all but unknown, and very few engineering students could take advantage of such a meagre scientific education as was then available. He was a striking example of what he himself said of some distinguished engineers :—"That they literally became such because they could not help it." With Bramwell the taste for engineering was innate and supreme. Study was not congenial to him ; his extensive and varied knowledge was mainly the outcome of personal observation and experience.

After some years' varied experience in different engineering workshops he commenced practice on his own account in 1853. He soon made his mark ; but, as he especially shone in debate, where his judgment was rarely at fault, and he brought shrewd common sense to bear with happy flashes of wit and apt practical illustrations, he was irresistibly drawn from the constructive to the legal side of his profession, in which he received no little advantage from his powerful voice and his commanding presence. In giving evidence, Bramwell was remarkably able, and as an arbitrator his judgments were clear, judicial, and marked by legal acumen. In one or other capacity his services were in much demand during the last thirty or forty years. He was chosen President of the Institution of Mechanical Engineers in 1874, and, ten years later, President of the Institution of Civil Engineers. He was President of the British Association at its meeting at Bath in 1888. He became one of

our Fellows in 1873, and served on the Council in 1877-1878. On the retirement of Sir William Bowman, he was elected Honorary Secretary of the Royal Institution. Honorary degrees were conferred upon him by the Universities of Oxford, Cambridge, Durham, and Montreal. In 1889 Queen Victoria bestowed upon him the honour of a baronetcy.

George Johnston Allman was born in Dublin in 1824. He entered Trinity College at an early age, and at the honour degree examination, in 1843, he obtained Senior Moderatorship and a gold medal in mathematics. A few years later he was elected to the Professorship of Mathematics in Queen's College, Galway, a post which he held for nearly forty years, until his retirement in accordance with the age limit. His most important works were a paper, "On some Properties of the Paraboloids," and a series of papers on the history of Greek mathematics, which formed the basis of his celebrated book "Greek Geometry from Thales to Euclid." He was elected a Fellow of the Society in 1884.

The name of Dr. Isaac Roberts will always be associated with the photography of the heavenly bodies. He early showed his love for physical science. His first scientific paper was on the wells and water of Liverpool, where he resided; and in the following year, 1870, he was elected a Fellow of the Geological Society. Other papers followed on underground waters, especially with respect to their oscillations in porous strata. He soon directed his principal attention to Astronomy, and erected an observatory near Liverpool. At first he contemplated photographing the whole northern heavens, but when an astrographic chart and catalogue for both hemispheres were undertaken by an international co-operation of Observatories, with great prescience he decided to devote himself to photographing star-clusters and nebulae. Finding the neighbourhood of Liverpool unfavourable for such work, after a long personal examination of various sites, he erected an observatory on Crowborough Hill, where, during thirteen years, he secured the splendid series of astronomical photographs, bringing to light a wealth of unsuspected detail, which have largely aided in the recent extension of our knowledge of nebulae and star-clusters. Two volumes containing reproductions of these photographs were published by Dr. Roberts at his own expense, and widely distributed among astronomers. He was elected to our Fellowship in 1890. In 1892 Trinity College, Dublin, conferred upon him the honorary degree of D.Sc.; three years later he received the gold medal of the Royal Astronomical Society.

To his many friends the sudden death of Sir Clement le Neve Foster came as a very painful shock. He was educated in France, and obtained the degree

of Bachelor of Science of the University of France at the early age of sixteen. He then entered the Royal School of Mines, where in two years he achieved the remarkable distinction of securing the Associateship in the Mining, Metallurgical, and Geological divisions, as well as the Duke of Cornwall's Scholarship and the Forbes Medal. In 1872 he was appointed H.M. Inspector of Mines. He succeeded, in 1890, Sir Warrington Smyth as Professor of Mining at the Royal College of Science, and the Royal School of Mines. He became a Fellow of our Society in 1892. On the King's birthday, last year, he received the honour of Knighthood. During his twenty-nine years' Government Inspectorship, Sir Clement did much to ameliorate the lot of the miner, and to establish metal mining on a scientific basis.

Quite recently the Society has suffered a further loss in the unexpected death of Dr. McClean, who, by his wisely considered benefactions, as well as by his personal work, has contributed not a little to the increase of natural knowledge. Having retired thirty-four years ago from professional work as an engineer, he built an astronomical observatory at his house at Tunbridge Wells, and devoted himself to photo-spectroscopic work on the sun and stars. His photographic spectra of all stars above the $3\frac{1}{2}$ magnitude appeared in our *Transactions*, in which he showed the presence of oxygen in connection with helium in certain stars. His benefactions to Science are of two kinds. In 1890 he founded the Isaac Newton Studentships at Cambridge for the promotion of the study of Astronomy and Astronomical Physics; while, on the practical side, ten years later, he made a most generous gift of valuable instruments to the Royal Observatory at the Cape of Good Hope. He has crossed the great bar, to the deep sorrow of his many friends, and to the great regret of all men of science.

During the last few years a very large amount, increasing each year, of work outside the reading, discussion, and printing of papers, of a more or less public character, has been thrown upon the Royal Society—so large indeed as at present to tax the Society's powers to the utmost. A not inconsiderable part of this work has come from the initiation by the Society itself of new undertakings, but mainly it has consisted of assistance freely given, at their request, to different Departments of the Government on questions which require expert scientific knowledge, and which involves no small amount of labour on the part of the Officers and Staff, and much free sacrifice of time and energy from Fellows, in most cases living at a distance.

There is little doubt that this largely-increased amount of public work has arisen, in part naturally from the greater scientific activity of the present day,

but also, and to a greater extent, from the fuller recognition by the Government and the public of the need for scientific advice and direction in connection with many matters of national concern.

It may not be inopportune, therefore, for me to say a few words on the advisory relation in which the Society has come to stand to the Government, and to review very briefly the great work which the Society has done, and is doing, for the Nation.

Among Academies and Learned Societies the position of the Royal Society is, in some respects, an exceptional one. In the British dominions it holds a unique position, not only as the earliest chartered scientific Society, but in its own right, on account of the number of eminent men included in its Fellowship, and the close connection in which it stands, though remaining a private institution, with the Government. The Royal Society is a private learned body, consisting of a voluntary and independent association of students of Science united for the promotion of Natural Knowledge at their own cost. It asks for no endowment from the State, for it could not tolerate the control from without which follows the acceptance of public money, nor permit of that interference with its internal affairs which, as is seen in some foreign academies, is associated with State endowment. In one particular case, in which it can receive aid without any loss of independence, the Society gratefully acknowledges its indebtedness to the State. About 1780 the Society received a communication from the Government offering to provide apartments for the Society at Somerset House; these were exchanged, in 1857, for rooms in old Burlington House; after its rebuilding, in 1873, the Society moved into the apartments which it now occupies. It should not be forgotten that nearly a century before the opening of the British Museum in 1759, the Royal Society's Museum, or Repository as it was called, enjoyed the prestige of being regarded as the most important Museum in London, and must have been of great use to men of science, and have aided materially in promoting and disseminating the knowledge of natural history. The apartments offered to the Society at Somerset House were quite insufficient in capacity and in number to receive the Society's Museum, and in consequence, this collection, which had been carefully maintained not only from the scientific side, but also with reference to the commercial value and importance of the foreign objects received, especially of the valuable zoological specimens frequently sent by the Hudson's Bay Company from their territories, was presented by the Society to the Nation, a not unworthy acknowledgment, on the Society's part, of the Government's gift of apartments. This collection has not been kept separate, but is now

hopelessly dispersed among the thousands of specimens which crowd the halls of our National Museum. Some specimens, however, in comparative anatomy, preserved in the Museum of the College of Surgeons, are duly entered in the catalogue as having belonged originally to the Royal Society's Museum.

Besides the grant of apartments in Somerset House, and subsequently in Burlington House, the Society has received no pecuniary support from Government, nor assistance of any kind, with one exception to be mentioned further on, beyond the grant by Charles II. shortly after its incorporation, of Chelsea College and the lands appertaining to it; a gift which proved much less valuable than appeared from the parchments. Claimants at once came forward for portions of the estate, and the property was in so unsettled a state as to title, and so much out of repair, that after much money had been spent on repairing the College and great exertions made in vain to procure a tenant, the President was authorised to sell the estate to the King for the sum of £1,300; the Council voting their thanks to him for "thus disposing of a property which was a source of continual annoyance and trouble to them." To the extent of this sum the Society's funds were enriched by the royal gift.

The grants of £4,000 and £1,000 now received annually by the Royal Society from the Government are not applicable to its own needs, but are placed in its hands in trust for grants in aid of the prosecution of scientific research, and of the publication of scientific papers; indeed, with the exception of part of the publication grant, are so far from being of the nature of a State bounty, that the careful administration of these grants brings no light burden upon the Society.

It may not be generally known that the Royal Society just missed becoming a richly-endowed Society. Charles II.'s interest in the young Society did not end with the grant of a Charter of Incorporation, for in 1662 he addressed a letter, written with his own hand, to the Duke of Ormonde, then Lord Lieutenant of Ireland, recommending the Royal Society for a "liberal contribution from the adventurers and officers of Ireland for the better encouragement of them in their designs." That is to say, in the new settlement in that country, on the Restoration, of the confiscated estates of such persons as by the King's declaration were disqualified. The Royal Society had but a poor chance, notwithstanding the King's letter, of coming in for a portion of these so-called "fractions," when so many high families were cheated of their rights, and the Duke's own estates, through his methods of adjudication, increased from £7,000 to £80,000 per annum. Sir

William Petty, in a document preserved in the archives of the Society, estimates the value of the lands granted by the King to the Society, but not received by them, "as a great matter, but I know not what."

It is on record that the non-fulfilment of the King's generous intentions towards the Society did not damp the philosophic ardour of the Fellows; indeed, it is a question on which opinions may widely differ whether the rich endowment of the Society, almost from its very birth, would have increased its scientific success. We must not forget that, in the case of institutions as well as of individuals, the powerful and healthy stimulus to the exertion needful for success which arises from the necessity of coping with and overcoming difficulties, whether of a monetary or other kind. In no small degree was due to the personal favour with which Charles II. regarded the Society, the exceptional position it early took up, and which it still holds to-day, of a private institution supported and controlled from within, which, at the same time, is acknowledged by the State as the authoritative national representative of Science in this country, and from time to time consulted as such.

The first royal act which distinctly gave this representative character to the newly chartered Society appears to have been the King's declaring his pleasure on the 15th October, 1662, "that no patent should pass for any philosophical or mechanical invention until examined by the Society." This personal recognition by the King of the national position of the Society was followed and confirmed a few years later by a request from the department of the Admiralty for assistance from the Royal Society in raising some ships sunk off Woolwich. The Council replied that, though they would have great pleasure in affording all assistance in their power by advice, the want of funds rendered it impossible for them to provide the necessary machinery.

From that time down to the present the Royal Society, while remaining a purely private institution for the promotion of Natural Knowledge, has been regarded by the Government as the acknowledged national scientific body, whose advice is of the highest authority on all scientific questions, and the more to be trusted on account of the Society's financial independence; a body, which, through its intimate relations with the learned societies of the Colonies, has now become the centre of British Science. The Society's historical position and the scientific eminence of its Fellows have made it naturally the body which the scientific authorities of foreign countries regard as representing the Science of the Empire, and with which they are anxious to consult and to co-operate, from time to time, on scientific questions of international importance.

On their part, the Fellows of the Royal Society, remembering that the promotion of Natural Knowledge is the great object for which it was founded and still exists, and that all undertakings in the home and in the State, since they are concerned with Nature, can be wisely directed and carried on with the highest efficiency only as they are based upon a knowledge of Nature, have always recognised the fundamental importance of the Society's work to national as well as to individual success and prosperity, and their own responsibility as the depositories of such knowledge. They have always been willing, even at great personal cost, ungrudgingly to afford any assistance in their power to the Government on all questions referred to them which depend upon technical knowledge, or which require the employment of scientific methods. In particular the Society has naturally always been eager to help forward, and even to initiate, such national undertakings as voyages of observation or of discovery of any kind, or for the investigation of the incidence of disease, which have for their express object the increase of Natural Knowledge.

At the same time, as the Society is dependent upon the voluntary help of its Fellows, whose time is fully occupied with their own work, the Society may reasonably expect the Government not to ask for assistance on any matters of mere administration that could be otherwise efficiently provided for. The hope may be expressed that in the near future, with increased official provision in connection with the recognition of Science, the relation of the Society to the Government may not extend beyond that of a purely advisory body, so that the heavy responsibilities now resting upon it, in respect of the carrying out of many public undertakings on which its advice has been asked, may no longer press unduly, as they certainly do at present, upon the time and energy of the Officers and Members of Committees. The Society regards this outside work, important as it is, as extraneous, and therefore as subordinate, and would not be justified in permitting such work to interfere with the strict prosecution of pure natural science as the primary purpose of the Society's existence, upon which, indeed, the Society's importance as an advisory body ultimately depends.

The array of national undertakings of which the Society has been wholly or in part in charge, or to which it has given advice or assistance from time to time, is so very great that any attempt to point out, even in broad outline, the more important of the directions in which the Society's influence has been actively employed for the public service, must necessarily be fragmentary and very incomplete. On this occasion it is not possible to do more than to give, in a few sentences, a rapid presentation of a few typical examples of the Society's public work.

It must be borne in mind that the bare statement in a few sentences of the public work accomplished by the Society fails altogether to bring before the imagination an adequate conception of the large amount of free labour ungrudgingly given by those Fellows who composed the several committees to which the work was entrusted.

Going back to the first century of the Society's existence, the work done for the National Observatory at Greenwich may be fairly taken as typical of the Society's outside activity at that time. It is not too much to say that the Observatory owes, in no small degree, its early efficiency and the high position it soon reached, to the advice and the energetic action on its behalf of the Royal Society. The Observatory, at the time it was placed, in 1710, by Queen Anne in the sole charge of the Society, was without instruments, except such as Flamsteed had himself supplied. Immediately on taking charge, the Society appointed a Committee which visited Greenwich, and, as a result, sent in an application to the Ordnance Office, but at the time unsuccessfully, for the new instruments which were absolutely essential for properly carrying on the work of an observatory. The little interest taken by the Government of that day in Science is manifest from the answer received from the Ordnance Office, "that they had never been at any charge for instruments, but only for repairing the house and paying Mr. Flamsteed's salary." The Society persevered, and when, in 1720, Halley succeeded Flamsteed, was successful in persuading the Government to provide a few of the more necessary instruments. At a little later date the Society induced the Government to expend £1,000 on instruments, to be constructed by Graham and Bird. When George III. came to the throne he re-appointed the Society as sole visitors, and ordered the Astronomer Royal to obey the regulations drawn up by the Council, and commanded the Master General of Ordnance to furnish such instruments as the Council should think necessary for the Observatory. In the list of these instruments is mentioned a ten-foot telescope of Dollond's "new invention." Further, it was in answer to a petition from the Royal Society that the King gave orders for the printing of the Observations made at the Observatory. At a later date the Society called on the Government to advance funds to establish magnetical observatories at Greenwich, and in various parts of the British dominions, with the result that in a few years no fewer than forty magnetical establishments were in full activity.

In connection with the Observatory may be mentioned the considerable share which the Society took in bringing about the important alteration of the Calendar, known as the Change of Style, which took place in 1752. The

Bill was drawn up by Peter Davall, the Secretary of the Society, aided and supported by Lord Macclesfield, who became President the same year. The change was approved and assisted by the actual President, Martin Folkes. The feeling of the people was so strongly against the change that the illness and death of Bradley, who as Astronomer Royal had assisted the Government with his advice, which took place not long afterwards, were popularly attributed to a judgment from Heaven.

Very brief must be the mention of some of the other works in the public service which were carried out at a no small cost of labour to the Fellows of the Society.

About 1750, the Lord Mayor of London, two of the Judges and an Alderman, having died in one year from jail-fever caught at the Old Bailey Sessions, the Society was called upon for advice and assistance. A committee was appointed to investigate the wretched state of ventilation in jails. A ventilator, invented by one of the committee, was erected in Newgate, reducing at once the number of deaths from eight a week to about two a month. Of the eleven workmen employed to put up the ventilator, seven caught the fever and died.

At the request of the Government, committees were appointed to consider the best form of protection of buildings, and, later on, of ships at sea, from lightning.

The Society took a very active part in the measurement of a degree of latitude, afterwards in the length of a pendulum vibrating seconds in the latitude of London, and in the comparison of the British Standards with the Linear Measure adopted in France. A committee was appointed to compare the Society's Standard yard with that of the Exchequer. Later, in 1834, when the Standard yard was lost in the destruction by fire of the Houses of Parliament, a Commission (all the members of which were Fellows of the Royal Society) was appointed to consider the steps to be taken for the restoration of the Standards.

It was at the instance of the Council of the Society, who petitioned George III. for the necessary funds, that the King gave his consent to a geodetical survey in 1784, with the immediate object of establishing a trigonometrical connection between the Observatories of Greenwich and Paris. The work, under General Roy, for which the Copley Medal was awarded to him, served as a basis for the operations of a more extensive nature, embracing a survey of the British Islands, which were commenced in 1791.

Since its foundation the Society has taken an active part in many

important expeditions for scientific and geographical exploration, and for magnetical and astronomical observations, in some cases taking the initiative by memorializing the Government for the necessary assistance by grants of money, the use of ships, or otherwise. Among these may be mentioned the expeditions sent out for the observation of the Transits of Venus in 1761, and in 1769.

The importance of Antarctic exploration, for which the recent National Expedition has recently been promoted jointly with the Royal Geographical Society, was fully understood by the Royal Society nearly a century and a half ago. In 1771, an expedition having for its principal object the exploring of high southern latitudes with the view of ascertaining the existence of a great Antarctic Continent, was strongly and successfully urged on the Government by the Society. The expedition under Captain Cook sailed the following year. On its return three years later, after having circumnavigated the globe, the Copley Medal was awarded to Captain Cook for the means he had taken to preserve the health of his crew.

In 1817, a letter was addressed by Sir Joseph Banks, on the part of the Council, to Lord Melville urging that an expedition of discovery should be sent out for determining the practicability of a North-West Passage. The Lords of the Admiralty gave orders for the fitting out of four vessels, and invited detailed instructions from the Royal Society for the guidance of the officers. The Council recommended Colonel, then Captain, Sabine to proceed with the North-West Expedition, and Mr. Fisher to accompany the Polar one. The expedition failed to procure geographical results of importance, but it was far from fruitless, for the magnetical observations brought back by Sabine were an addition of real value to physical science.

This expedition was followed by another two years later under Parry, which resulted in the discovery of the Strait called after Barrow, then Secretary to the Admiralty.

A later Polar Expedition, under Captains Parry and Ross in 1827, was promoted by the Royal Society, and brought home valuable magnetical observations, which were printed in the Society's Transactions.

At home, it was through the Society's influence that Dr. Maskelyne, the Astronomer Royal, was able to make observations in Scotland for the purpose of deducing the density of the earth. Dr. Hutton undertook the laborious task of working up the data, the whole expenses being borne by the Society.

These few examples, inadequate as they are, must suffice on this occasion to remind us of the many labours during two centuries and a half undertaken

by the Society for the public good. I pass now at once to some of the many objects of public concern, which are at the present time either directly promoted, or assisted by the Society.

The establishment in this country of a National Physical Laboratory for the purpose of bringing scientific knowledge to bear practically upon the industries and commerce of the nation, was due in no small measure to the action of the Society, and has certainly thrown upon it much additional permanent responsibility. The necessity for such an Institution in this country, which was clearly shown by the marked influence of a similar Institution on the improvement of technical science and the manufacturing interests of Germany, had been already strongly advocated by individual Fellows; in particular, by Sir Oliver Lodge at Cardiff in 1891, and Sir Douglas Galton at Ipswich five years later; but the first practical step towards its realisation was taken by the Council in 1896, when they decided that the Royal Society should join the British Association and other kindred Societies in a Joint Committee, under the Chairmanship of the President of the Royal Society, to take such action as they find desirable.

In the following year, this Committee waited upon Lord Salisbury, who was then Prime Minister, and, as a result, a Treasury Committee was appointed by the Chancellor of the Exchequer, with Lord Rayleigh as Chairman, to consider the desirability of establishing a National Laboratory. That Committee, after hearing witnesses and visiting Germany, reported strongly and unanimously in favour of such a national Institution. In 1898, a communication was received from the Treasury expressing "the hope that the Royal Society will be willing to add to the already great services rendered by them to the Government and public of the United Kingdom, by consenting to undertake the new responsibilities now sought to be imposed upon them" in connection with the new Institution. The Council accepted the important trust, under which the "ultimate control of the Institution is vested in the President and Council of the Royal Society, who in the exercise thereof may issue from time to time such directions as they may think fit to the General Board and Executive Committee." The income and all other property is vested in the Royal Society for the purposes of the Institution. The Laboratory, which was formally opened by H.R.H. the Prince of Wales in March, 1902, has already made remarkable progress under its energetic Director. During the present year the attention of the Prime Minister has been called to the very great importance to the national industries of an immediate grant for new buildings and a more adequate instrumental equipment, and of a larger annual endowment.

It is not too much to say that men of Science of all countries are under no small obligation to the Royal Society for their Catalogue of Scientific Papers which have appeared in all parts of the world since the beginning of the last century. This great work, to which immense labour has been given gratuitously and without stint by Fellows during the past forty years, will be carried down to the close of the century, and will consist of two parts: an Authors' Catalogue, and a Catalogue of Subjects. Encouraged by a donation from Mr. Andrew Carnegie, and the noble liberality of Dr. Ludwig Mond and other Fellows, the Council decided to proceed with the completion of the Catalogue, in the hope of further donations from Fellows and others as the work advances.

It was obvious that to continue permanently to prepare and publish catalogues of the rapidly increasing output of scientific literature would be wholly beyond the means of any one Society, and was an undertaking so vast as to require organized international co-operation for success. In 1893, a letter, signed by seventeen Fellows, was addressed to the President, asking that steps might be taken to provide for the continuation of the Society's Catalogue from the beginning of the century by adequate international co-operation. A Committee was appointed, which reported in favour of an international conference on the subject. Three conferences were held successively in 1896, 1898, and 1900. It is scarcely possible to convey an adequate conception of the arduous and prolonged labours of these conferences, and of the numerous meetings of committees held in connection with them. The Society may well feel great satisfaction that a work of such magnitude, and of so great moment to all scientific workers, which was initiated by itself, was taken up with such remarkable accord by the scientific world. The organization consists mainly of a Central Bureau in London under the Royal Society, in connection with Regional Bureaus, established in thirty countries for collecting material in the form of catalogue slips, and transmitting them to the Central Bureau. The Royal Society has taken upon itself practically the financial responsibility of the undertaking, making contracts in its own name with a printer and a publisher, the latter undertaking the technical duties as agent for the Society, which is its own publisher. The first year's issue of the catalogue has appeared, dealing in twenty-one volumes with the seventeen sciences decided upon by the conference.

The International Association of Academies, the realization for the first time of the great scientific idea of a Universal Academy, open without restriction of language or of country to every nation under heaven, owes its

establishment to the initiative of the Royal Society. In 1897, the Royal Society was invited to send representatives to a Conference of a Union of German Academies and Societies which met from time to time. The Society sent delegates, but declared that the Society's permanent adhesion to any such association must be conditional on its being made truly international in character. The principle of an international association of learned Societies suggested by the Royal Society, was accepted, and a Conference was held at Wiesbaden in 1899 for the purpose of taking steps for the formation of such an association. Statutes were drawn up and arrangements made for the holding of the first General Assembly in Paris in 1901.

The primary objects of the Association are the initiation and promotion of scientific undertakings of general interest and of universal concern to mankind, especially of such matters as are outside the power of a single Academy and require for their promotion the assistance of the Governments represented by the Association. Indirectly by its triennial General Assemblies in different countries, it should become an instrument of no mean power for the promotion of the brotherhood of mankind and for hastening the day

“ When the war drums throb no longer and the battle flags are furl'd,
In the Parliament of man, the Federation of the world.”

The Association, as now constituted, consists of twenty Academies and learned Societies of Europe and America. The second General Assembly of the Association was held this year in London under the auspices of the Royal Society, which, as directing Academy, had had general charge of the conduct of its business during the last three years. The Section of Letters met under the direction of the newly-founded British Academy.

The Society has accepted heavy responsibilities at the instance of the Government in respect of the control of scientific observations and research in our vast Indian Empire. In 1899, the India Office inquired whether the Royal Society would be willing to meet the wishes of the Indian Government by exercising a general control over the scientific researches which it might be thought desirable to institute in that country. A Standing Committee was appointed in consequence by the Council for the purpose of giving advice on matters connected with scientific enquiry, probably mainly biological, in India, which should be supplementary to the Standing Observatories Committee which was already established at the request of the Government as an advisory body on astronomical, solar, magnetic, and meteorological observations in that part of the Empire.

An investigation, onerous indeed, but of the highest scientific interest and

of very great practical importance, has been carried on by a series of Committees successively appointed at the request of the Government for the consideration of some of the strangely mysterious and deadly diseases of tropical countries. In 1896 a Committee was appointed at the request of the Colonial Secretary to investigate the subject of the Tsetse Fly disease in South Africa. Two years later Mr. Chamberlain, Secretary of State for the Colonies, requested the Society to appoint a Committee to make a thorough investigation into the origin, the transmission, and the possible preventives and remedies of tropical diseases, and especially of the malarial and "Blackwater" fevers prevalent in Africa, promising assistance, both on the part of the Colonial Office and of the Colonies concerned. A Committee was appointed, and, under its auspices, skilled investigators were sent out to Africa and to India. In the case of the third Committee the Society itself took the initiative. An outbreak in Uganda of the disease, appalling in its inexorable deadliness, known as "Sleeping Sickness" having been brought to the knowledge of the Society, a deputation waited upon Lord Lansdowne at the Foreign Office, asking him to consider favourably the despatch of a small Commission to Uganda to investigate the disease. He gave his approval, and a Commission of three experts, appointed on the recommendation of the Committee, was sent out to Uganda, £600 being voted out of the Government Grant towards the expenses of the Commission.

The investigations in tropical diseases, promoted and directed by these Committees, have largely increased our knowledge of the true nature of these diseases, and, what is of the highest practical importance, they have shown that their propagation depends upon conditions which it is in the power of man so far to modify, or guard against, as to afford a reasonable expectation that it may be possible for Europeans to live and carry on their work in parts of the earth where hitherto the sacrifice of health, and even of life, has been fearfully great. A general summary of the work already done on Malaria, especially in regard to its prevention, and also on the nature of "Blackwater" Fever, has been published in a Parliamentary paper, which records Mr. Chamberlain's acknowledgment to the Royal Society for its co-operation in the work undertaken by the Colonial Office. Our Reports on Sleeping Sickness up to this time form four parts of a separate publication giving evidence in support of the view that this deadly disease is caused by the entrance into the blood, and thence into the cerebro-spinal fluid, of a species of *Trypanosoma*, and that these organisms are transmitted from the sick to the healthy by a kind of tsetse fly, and by it alone; Sleeping Sickness is in short, a human tsetse fly disease.

In 1897, the Council was requested to assist the Board of Trade in drawing up Schedules for the establishment of the relations between the Metric and the Imperial Units of Weights and Measures. A Committee was appointed, which, after devoting much time and attention to the matter, drew up Schedules which were accepted by the Board of Trade and incorporated in the Orders of Council.

A Coral Reef Committee has been in active existence for some years, and has directed the attempts to pierce, by boring, the atoll of Funafuti, towards the expenses of which grants have been made by the Council. The results of the work have appeared in a large volume, giving a description of the whole core from the points of view of the naturalist and the chemist; and a list, with critical remarks, of the species of animals and plants collected.

Soon after the reports were received of the appalling volcanic eruptions and the loss of life which took place in the West Indies in 1902, the Council received a letter from Mr. Chamberlain to ask if the Society would be willing to undertake an investigation of the phenomena connected with the eruptions. The Council, considering that such an investigation fell well within the scope of the objects of the Society, organized a small Commission of two experts, who left England for the scene of the eruption eleven days only after the receipt of Mr. Chamberlain's letter; the expenses being met by a grant of £300 from the Government Grant Committee. Six weeks were spent in the Islands, including Martinique, by the Commission, which was successful in securing results of great scientific interest. A preliminary report was published at the time, and a full report has since appeared in the "Transactions."

Time forbids me to do more than mention the successive expeditions sent out by the Society, conjointly with the Royal Astronomical Society, for the observation of total solar eclipses; and the onerous work thrown upon the Society for several years in connection with the National Antarctic Expedition, undertaken jointly with the Royal Geographical Society, which has this year returned home crowned with success as regards the latter; but the Society's labours are not at an end, for the prolonged and responsible task of the discussion and publication of the scientific results of the Expedition is still before them.

In addition to the numerous undertakings, of which some examples have been given, in which the influence and work of the Society have been exercised for national or public objects, there are a number of other ways in which the Society makes its influence continually felt and of which the responsibilities are always with it. The Society is represented by the

President, as an *ex-officio* elector, in the election of eight scientific Professorships at the Oxford University, and one Professorship at Cambridge. The President is also *ex-officio* a trustee of the British Museum, and of the Hunterian Museum, and a Governor of the City and Guilds of London Institute. The Society has a voice, through a representative Fellow chosen by the Council, on the Governing bodies of the Imperial Institute, the Lister Institute of Preventive Medicine, Sir John Soane's Museum, Eton, Rugby, Harrow, Winchester, and four other Public schools, and the Advisory Board for Military Education. The Council of the Society are electors of four members of Lawes' Agricultural Trust, and are nominators of the members of the Meteorological Council. The Society is represented by the President and six of the Visitors on the Board of the Greenwich Observatory. One of the four sets of copies of the Standard Weights and Measures is held in custody by the Society. There is also a Committee for systematic work in Seismology.

To the Royal Society is entrusted the responsible task of administering the annual Government Grant of £4000 for the purpose of scientific research, and a grant of £1000 in aid of the publication of scientific papers.

In addition to these permanent responsibilities, which are always with the Society, its advice and aid are sought from time to time both by the Government and by Scientific Institutions at home and abroad, in favour of independent objects of a more or less temporary character, of which, as examples, may be taken the recent action of the Society for the purpose of obtaining Government aid for the continuation through Egypt of the African Arc of Meridian, and for the intervention of the Government to assist in securing the fulfilment of the part undertaken by Great Britain in the International Astrographic Catalogue and Chart.

Upon the present Fellows falls the glorious inheritance of unbounded free labour ungrudgingly given during two centuries and a-half for the public service, as well as of the strenuous prosecution at the same time of the primary object of the Society, as set forth in the words of the Charters: "The promotion of Natural Knowledge." The successive generations of Fellows have unsparingly contributed of their time to the introduction and promotion, whenever the opportunity was afforded them, of scientific knowledge and methods into the management of public concerns by Departments of the Government. The financial independence of the Royal Society, neither receiving, nor wishing to accept State aid for its own private purposes, has enabled the Society to give advice and assistance which, both with the Government and with Parliament, have the weight and finality of a wholly disinterested opinion. I may quote here the words of a recent letter from

H.M. Treasury :—" Their Lordships have deemed themselves in the past very fortunate in being able to rely, in dealing with scientific questions, upon the aid of the Royal Society, which commands not only the confidence of the scientific world, but also of Parliament."

In the past the Royal Society has been not infrequently greatly hampered in giving its advice, by the knowledge that the funds absolutely needed for the carrying out of the matters in question in accordance with our present scientific knowledge would not be forthcoming. Though I am now speaking on my own responsibility, I am sure that the Society is with me, if I say that the expenditure by the Government on scientific research and scientific institutions, on which its commercial and industrial prosperity so largely depend, is wholly inadequate in view of the present state of international competition. I throw no blame on the individual members of the present or former Governments; they are necessarily the representatives of public opinion, and cannot go beyond it. The cause is deeper, it lies in the absence in the leaders of public opinion, and indeed throughout the more influential classes of society, of a sufficiently intelligent appreciation of the supreme importance of scientific knowledge and scientific methods in all industrial enterprises, and indeed in all national undertakings. The evidence of this grave state of the public mind is strikingly shown by the very small response that follows any appeal that is made for scientific objects in this country, in contrast with the large donations and liberal endowments from private benefaction for scientific purposes and scientific institutions which are always at once forthcoming in the United States. In my opinion, the scientific deadness of the nation is mainly due to the too exclusively mediæval and classical methods of our higher public schools, and can only be slowly removed by making in future the teaching of Science, not from text-books for passing an examination, but, as far as may be possible, from the study of the phenomena of Nature by direct observation and experiment, an integral and essential part of all education in this country.

I proceed to the award of the Medals.

COPLEY MEDAL.

The Copley Medal is awarded to Sir William Crookes, F.R.S., for his experimental researches in chemistry and physics, extending over more than fifty years. Ever since his discovery of the element thallium in the early days of spectrum analysis, he has been in the front rank as regards the refined application of that weapon of research in chemical investigation. Later, the discrepancies which he found in an attempt to improve weighings, by con-

ducting the operation in high vacua, were tracked out by him to a repulsion arising from radiation, which was ultimately ascribed by theory to the action of the residual gas. This phenomenon, illustrated by the radiometer, opened up a new and fascinating chapter in the dynamical theory of rarefied gases, which the genius of Maxwell, O. Reynolds, and others has left still incomplete. The improvements in vacua embodied in the Crookes tube led him to a detailed and brilliant experimental analysis of the phenomena of the electric discharge across exhausted spaces; in this, backed by the authority of Stokes, he adduced, long ago, powerful cumulative evidence that the now familiar cathode rays, previously described by C. F. Varley, must consist of projected streams of some kind of material substance. His simple but minutely careful experiments on the progress of the ultimate falling off in the viscosity of rarefied gases, from the predicted constant value of Maxwell, at very high exhaustions, gave, in Stokes' hands, an exact account of the trend of this theoretically interesting phenomenon, which had already been approached in the investigations of Kundt and Warburg, using Maxwell's original method of vibrating discs.

These examples, not to mention recent work with radium, convey an idea of the acute observation, experimental skill, and persistent effort, which have enabled Sir William Crookes to enrich physical science in many departments.

RUMFORD MEDAL.

The Rumford Medal is awarded to Prof. Ernest Rutherford, F.R.S., on account of his researches on the properties of radio-active matter, in particular for his capital discovery of the active gaseous emanations emitted by such matter, and his detailed investigation of their transformations. The idea of radiations producing ionization, of the type originally discovered by Röntgen, and the idea of electrified particles, like the cathode rays of vacuum tubes, projected from radio-active bodies, had gradually become familiar through the work of a succession of recent investigators, when Rutherford's announcement of a very active substance, diffusing like a gas with a definite atomic mass, emitted by compounds of thorium, opened up yet another avenue of research with reference to these remarkable bodies. The precise interpretation of the new phenomena, so promptly perceived by Rutherford, was quickly verified for radium and other substances, by various observers, and is now universally accepted. The modes of degradation, and the enormous concomitant radio-activity, of these emanations, have been investigated mainly by Rutherford himself, with results embodied in his treatise on Radio-activity and his recent

Bakerian Lecture on the same subject. It perhaps still remains a task for the future to verify or revise the details of these remarkable transformations of material substances, resulting apparently in the appearance of chemical elements not before present; but, however that may issue, by the detection and description of radio-active emanations and their transformations, Prof. Rutherford has added an unexpected domain of transcendent theoretical interest to physical science.

ROYAL MEDAL.

A Royal Medal is awarded to Prof. W. Burnside, F.R.S., on the ground of the number, originality, and importance of his contributions to Mathematical Science. The section of our "Catalogue of Scientific Papers" for the period 1883-1900, enumerates fifty-three papers by Prof. Burnside, the first dated 1885, and the "International Catalogue of Scientific Literature" thirteen more. His mathematical work has consisted largely of papers on the Theory of Groups, to which he has made most valuable additions. In 1897 he published a volume "On the Theory of Groups of Finite Order," which is a standard authority on that subject. Two recent papers on the same theory, published in 1903, may be specially mentioned. In one of these he succeeded in establishing by direct methods, distinguished by great conciseness of treatment, the important subsidiary theory of group-characteristics, which had been originally arrived at by very indirect and lengthy processes. In the other he proved quite shortly the important result that all groups of which the order is the product of powers of two primes are soluble.

Besides the treatise and papers relating to group theory, Prof. Burnside has published work on various branches of pure and applied mathematics. His work on automorphic functions dealt with an important and difficult special case which was not included in the theory of these functions as previously worked out. The paper on Green's function for a system of non-intersecting spheres was perhaps the first work by any writer in which the notions of automorphic functions and of the theory of groups were applied to a physical problem. He has also made important contributions to the Theory of Functions, Non-Euclidean Geometry, and the Theory of Waves on Liquids. His work is distinguished by great acuteness and power, as well as by unusual elegance and most admirable brevity.

ROYAL MEDAL.

The other Royal Medal is awarded to Col. David Bruce, F.R.S., who, since 1884, has been engaged in prosecuting to a successful issue researches into

the causation of a number of important diseases affecting man and animals. When he went to Malta in 1884 the exact nature of the widely-prevalent "Malta," "Rock," or "Mediterranean" Fever was entirely unknown. After some years' work at the etiology of this disease, he discovered in 1887 the organism causing it, and succeeded in cultivating the *Micrococcus melitensis* outside the body. This discovery has been confirmed by many other workers, and is one of great importance from all points of view, and perhaps more especially as, thanks to it, Malta Fever can now be separated from other diseases, *e.g.*, typhoid, remittent, and malarious fevers, with which it had hitherto been confounded.

During the next few years he was engaged in researches of value on Cholera, and on methods of immunisation against this disease. He also carried out some work on the Leucocytes in the Blood, published in the "Proceedings of the Royal Society," 1894.

In 1894 he was requested by the Governor of Natal to investigate the supposed distinct diseases of "Nagana" and the Tsetse Fly disease. In the short time of two months he made the most important discovery that these two diseases were one and the same, and dependent upon the presence of a protozoan organism in the blood known as a Trypanosoma. Some six months later Bruce was enabled to return to Zululand, and remained there two years, studying the disease and making the discovery that the Tsetse Fly acted as the carrier of the organism which caused it. He was thus the first to show that an insect might carry a protozoan parasite that was pathogenic. This observation was made in 1895.

Bruce not only determined the nature and course of "Nagana," but in addition he studied the disease in a large number of domestic animals, and also observed the malady in a latent form in the wild animals of South Africa. Subsequent observers have found but little to add to Bruce's work on this subject.

In 1900, Bruce was ordered to join a Commission investigating the outbreak of Dysentery in the Army in South Africa, and a great part of the laboratory work performed by this Commission was carried out by him.

In 1903, Col. Bruce went, at the request of the Royal Society, to Uganda, to investigate further the nature of Sleeping Sickness. It was very largely, if not entirely, owing to him that the work of the Royal Society's Commission was brought to a successful issue. At the time when he arrived, a Trypanosoma had been observed by Castellani in a small number of cases of this disease; thanks to Bruce's energy and scientific insight, these observations were rapidly extended, and the most conclusive evidence obtained, that in all

cases of the disease the *Trypanosoma* was present. He showed further that a certain Tsetse Fly, the *Glossina palpalis*, acted as the carrier of the *Trypanosoma*, and obtained evidence showing that the distribution of the disease and of the fly were strikingly similar.

Bruce has therefore been instrumental in discovering and establishing the exact nature and cause of three wide-spread diseases of man and of animals, and in two of these, Nagana and Malta Fever, he discovered the causal organism. In the third, Sleeping Sickness, he was not the first to see the organism, but he was quick to grasp and work out the discovery, and he made the interesting discovery of the carrier of the pathogenic organism, and thus discovered the mode of infection and of spread of the malady, matters of the highest importance as regards all measures directed to arrest the spreading of the disease. All this research work has been done whilst serving in the Royal Army Medical Corps, and engaged in the routine work of the Service.

DAVY MEDAL

The Davy Medal is awarded to Prof. W. H. Perkin, jun., F.R.S., for his masterly and fruitful researches in the domain of synthetic organic chemistry, on which he has been continuously engaged during the past twenty-five years.

Dr. Perkin's name is identified with the great advances which have been made during the past quarter of a century in our knowledge of the ring or cyclic compounds of carbon. Thus, in the year 1880, the cyclic carbon compounds known to chemists were chiefly restricted to the unsaturated groupings of six carbon atoms met with in benzene and its derivatives, whilst the number of compounds in which saturated carbon rings had been recognised was very limited, and it was indeed considered very doubtful whether compounds containing carbon rings with more or less than six atoms of carbon were capable of existence.

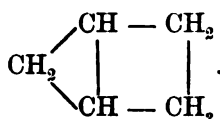
The starting point for Dr. Perkin's researches in this field of enquiry was his investigation of the behaviour of the di-halogen derivatives of various organic radicals with the sodium compounds of malonic, aceto-acetic, and benzoyl-acetic esters, which led to the synthesis of the cyclic polymethylene compounds up to those of hexamethylene, whilst heptamethylene derivatives were obtained by an adaptation of the well-known reduction of ketonic bodies leading to pinacones. The reactions thus introduced by Perkin are now classical, having proved themselves of the highest importance for synthetical purposes and having been instrumental in stimulating the further investigation of the cyclic compounds of carbon.

Dr. Perkin also extended the same methods to the synthetical formation of carbon rings of the aromatic series, obtaining by means of ingeniously designed reactions derivatives of hydrindonaphthene and tetrahydronaphthalene.

But whilst the above achievements depend mainly on happily conceived and brilliantly executed extensions of the malonic and aceto-acetic ester syntheses, Perkin has, by a remarkable development of the Frankland and Duppa reaction for the synthesis of hydroxyacids, been successful in building up the important camphoronic acid in such a manner as to place its constitution beyond doubt (1897).

Dr. Perkin has further devoted much attention to the important subject of the constitution of camphor, towards the elucidation of which he has contributed valuable experimental evidence embodied in a most important and elaborate paper, containing the results of many years' work in conjunction with numerous pupils, entitled "Sulphocamphylic acid and Isolauronic acid, with remarks on the Constitution of Camphor and some of its derivatives" (1898). Bearing on the same subject are later communications on camphoric acid and isocamphoronic acid.

About the year 1900, Perkin, in prosecuting his researches on the constitution of camphor compounds, succeeded in devising synthetical methods for the production of what he has termed "bridged rings," of which a simple example is furnished by the hydrocarbon dicyclopentane



The universal admiration of organic chemists has been called forth by these investigations; they reveal, indeed, a wonderful capacity for devising reactions which coerce carbon atoms to fall into the desired groupings.

Of other publications displaying not only extraordinary experimental skill but close reasoning and the power of interpreting results, mention may be made of Dr. Perkin's memorable researches on the constitution of dehydroacetic acid, berberine, brasilin, and hæmatoxylin respectively.

During the present year (1904), Dr. Perkin has made perhaps the most remarkable addition to the long list of his achievements by successfully synthesising terpin, inactive terpineol, and dipentene, substances which had previously engaged the attention of some of the greatest masters of organic chemistry.

In conclusion it may be stated that Professor Perkin is not only the author of the above and numerous other important researches which are outside the scope of this brief summary, but that he has also created a school of research in organic chemistry, which stands in the very highest rank.

DARWIN MEDAL.

The Darwin Medal is awarded to Mr. William Bateson, F.R.S., for his researches on heredity and variation.

Mr. Bateson began his scientific career as a morphologist, and distinguished himself by researches on the structure and development of *Balanoglossus*, which have had a far-reaching influence on morphological science, and which established to the satisfaction of most anatomists the affinity of the *Enteropneusta* to the Chordate phylum. Dissatisfied, however, with the methods of morphological research as a means of advancing the study of evolution, he set himself resolutely to the task of finding a new method of attacking the species problem. Recognising the fact that variation was the basis upon which the theory of evolution rested, he turned his attention to the study of that subject, and entered upon a series of researches which culminated in the publication in 1894 of his well-known work, entitled "*Materials for the Study of Variation, etc.*" This book broke new ground. Not only was it the first systematic work which had been published on variation, and, with the exception of Darwin's "*Variation of Animals and Plants under Domestication*," the only extensive work dealing with it; but it was the first serious attempt to establish the importance of the principle of discontinuity in variation in its fundamental bearing upon the problem of evolution, a principle which he constantly and successfully urged when the weight of authority was against it. In this work he collected and systematised a great number of examples of discontinuous variation, and by his broad and masterly handling of them he paved the way for those remarkable advances in the study of heredity which have taken place in the last few years, and to which he has himself so largely contributed. He was the first in this country to recognise the importance of the work of Mendel, which, published in 1864, and for a long time completely overlooked by naturalists, contained a clue to the labyrinth of facts which had resulted from the labours of his predecessors. He has brought these results prominently forward in England in his important reports to the Evolution Committee of the Royal Society, and in papers before the Royal and other Societies, and also before horticulturists and breeders of animals. He has gathered about him a distinguished body

of workers, and has devoted himself with great energy and with all his available resources to following out lines of work similar to those of Mendel. The result has been the supporting of Mendel's conclusions and the bringing to light of a much wider range of facts in general harmony with them. It is not too much to say that Mr. Bateson has developed a school of research to which many biologists are now looking as the source from which the next great advance in our knowledge of organic evolution will come.

SYLVESTER MEDAL.

The Sylvester Medal is awarded to Georg Cantor, Professor in the University of Halle, on account of his researches in Pure Mathematics. His work shows originality of the highest order, and is of the most far-reaching importance. He has not only created a new field of mathematical investigation, but his ideas, in their application to analysis, and in some measure to geometry, furnish a weapon of the utmost power and precision for dealing with the foundations of mathematics, and for formulating the necessary limitations to which many results of mathematics are subject.

In 1870 he succeeded in solving a question which was then attracting much attention—the question of the uniqueness of the representation of a function by Fournier's series. The extension of the result to cases in which the convergence of the series fails, at an infinite number of suitably distributed points, led him to construct a theory of irrational numbers, which has since become classical. From the same starting point he developed, in a series of masterly memoirs, an entirely new branch of mathematics—the Theory of Sets of Points.

Having established the fundamental distinction between those aggregates which can be counted and those which cannot, Cantor showed that the aggregates of all rational numbers and of all algebraic numbers belong to the former class, and that the arithmetic continuum belongs to the latter class, and further, that the continuum of any number of dimensions can be represented point for point by the linear continuum. Proceeding with these researches he introduced and developed his theory of "transfinite" ordinal and cardinal numbers, thus creating an Arithmetic of the Infinite. His later abstract theory of the order-types of aggregates, in connection with which he has given a purely ordinal theory of the arithmetic continuum, has opened up a field of research of the greatest interest and importance.

HUGHES MEDAL.

The Hughes Medal is awarded to Sir Joseph Wilson Swan, F.R.S., for his invention of the incandescent electric lamp, and his other inventions and improvements in the practical applications of electricity. Not as directly included in the award, should be mentioned his inventions in dry-plate photography, which have so much increased our powers of experimental investigation.

*The Boring of the Simplon Tunnel, and the Distribution of
Temperature that was encountered.*

By FRANCIS FOX, M.Inst.C.E.

(Communicated by C. V. Boys, F.R.S. Received January 6,—
Read January 26, 1905.)

The construction of this great tunnel under the Swiss Alps, between Brigue in Switzerland in the valley of the Rhone, and Iselle in that of the Diveria in Italy, a distance of 19,730 metres, has been carried on upon such highly scientific lines, and has revealed such extraordinary results, that it has been thought desirable to submit them in the form of a communication to the Royal Society. They are likely to prove of considerable value and importance as regards the thermal condition of the region underlying that portion of the surface of the earth.

It is not necessary here to refer to the splendid organisation of the enterprise, nor to the humane arrangements for the welfare of the men ; but the rapidity with which the drilling has been effected, and the advance-headings driven forward, as also the excellent ventilation provided, have enabled much more trustworthy results to be obtained than would otherwise have been the case.

The Brandt hydraulic drill, by which a daily advance of 5·48 metres (18 feet) for months together, has been attained, has been described elsewhere ; but the fact of its rapid advance enables the temperature of the rocks to be recorded before the lapse of a considerable time during which the rocks would be cooling. On the other hand, the very excellent system

of ventilation, which has been provided, passes an enormous volume of fresh air along the galleries, thus tending to produce a lowering effect in temperature.

During the trimestral period of July, August, and September, 1904, the average volume of air introduced into the tunnel daily was as follows:—

From the Brigue portal	2,934,140	cub. metres
From the Iselle	2,361,310	"
Or a total of	5,295,450	"

equivalent to 33·9 cub. metres per second at Brigue and 27·3 cub. metres per second at Iselle. During this period the average temperature of the external air was 17°·5 C., that of the travelling air in the advanced headings being from 27°·1 to 29°·7 C.

As the advanced gallery was proceeded with, a series of holes were bored into the side of the tunnel, in a horizontal position, to a depth of 1·5 metres, at a distance apart of 1000 metres. Into each hole was introduced a permanent thermometer, from which observations were made and results recorded. It is not, of course, possible to place the thermometer in advance of the excavation, as it would be broken by the next "shot" in the blasting operations. It is, however, placed in position in the side wall as soon after the boring machine has gone forward as is possible. The effect of this, no doubt, is that a slight cooling of the rock occurs before the observation can be made, but this factor of error has been as far as possible allowed for in the diagram.

On the accompanying profile (fig. 1), which is drawn to natural scale, the squares being 1000 metres horizontal and vertical, is shown the position of the tunnel, with the height of the mountains above it throughout, and on the lower diagram are given the results of temperature observations, so that at a glance the heat curve may be compared with the corresponding mountain surface.

It will be observed that the maximum height of the Alps above the tunnel is 2135 metres (7005 feet), which is far greater than any depth previously attained; the maximum temperature of the rocks is 54°·5 C.

In order to show the rapid cooling of the rocks, so soon as perforation has taken place, I have selected four points on both sides, dated March, 1901, 1902, 1903, 1904; the explanation of one will suffice for the remaining three.

March, 1901 Up to that date observations had been taken from the entrance at Brigue to a distance of 4693 metres, and these are represented

SIMPLON TUNNEL



by the thick top line on the chart. But at that actual date, the readings between that point and the portal had been lowered by cooling, as represented by the "one dot and dash" line.

Similarly in March, 1902, when the distance of 6884 metres had been reached, the readings are indicated by a "two dot and dash" line.

In March, 1903, at a distance of 8930 metres, they are given by a "three dot and dash" line; and in March, 1904, at 10,140 metres, by a "four dot and dash" line.

At the southern or Iselle side of the Alps, it will be noticed that the temperature follows approximately the increasing altitude of the mountains, until a point is reached at about 2200 metres. From that point forward as the tunnel advanced the heat began to fall off, indicating some probable change; at about 4000 metres it fell rapidly, until at 4400 metres it attained the lowest point recorded throughout the tunnel, and the "Great Spring" of 800 litres per second (10,564 gallons per minute) was struck. The water when first encountered was under very high pressure, believed to be about 42 kilogrammes per square centimetre (600 lbs. to the square inch), but it now escapes under normal pressure, and with a temperature of about 13° C.

In consequence of the heat encountered in the extreme advanced headings under the centre of the Alps, resulting in high temperatures both in the air and in the water travelling along the tunnel from the "feeders," the dotted line of March, 1904, indicates a diminution in the cooling-off of the rocks on the north side between 2.6 kilometres and 8 kilometres; and between 1 kilometre and 2.6 kilometres, the thermometers actually register higher figures than were encountered in the original driving of the tunnel.

In like manner on the south side between 0 kilometre and 4.4 kilometres the cooling-off has been reduced.

In considering the rise of the Earth's temperature as progressive depths are attained from the surface, these phenomena at 4400 metres on the south side must be regarded as purely accidental, and as in no way affecting the general problem; they must, therefore, be discarded and not be allowed to affect in any way the calculations or conclusions.

There are many other disturbing factors which prevent any really definite law being laid down: much depends upon the inclination of the strata, whether horizontal, inclined, or vertical; whether synclinal, or anticlinal; the character of the rocks must also affect the problem considerably.

A point of some difficulty to ascertain, is the temperature which is to be assumed as existing near the surface in the high Alps. Where perpetual

snow prevails, it doubtless acts as a protection, and prevents radiation; and where snow lies during the long months of winter, the same results obtain to a modified degree. Probably at a depth of 6 to 9 metres below the surface the temperature remains nearly uniform, and it will be safe to assume it to be zero Centigrade (32° F.).

As we have a total height of 2135 metres (7005 feet) available, it will vitiate the results but to a very small extent, whether this be taken as 6, 9, or 12 metres. But assuming 10 metres to be the depth at which uniformity is to be found, we then have 2125 metres as corresponding to a rise of temperature of $54^{\circ}\cdot3$ C. (or $97^{\circ}\cdot7$ F.), giving a temperature gradient of 39 metres for 1° C. (71·5 feet for each degree Fahrenheit).

With the view to obtaining an average of the results, I have selected the altitudes and temperatures between 8 kilometres and 13 kilometres, and the temperature gradient thus obtained gives 37 metres per degree Centigrade, or 67·5 feet per degree Fahrenheit.

I was in hopes that I should have been able to report in this communication the successful and final perforation of the tunnel, but owing to the presence of very large "feeders" of hot water (46° C.) encountered at 9141 metres from the southern entrance, progress has been retarded.

At this date (December 22), however, there remains only a distance of 203 metres to be traversed before the headings meet, and a through passage is expected early in 1905, but this in no way modifies the temperature results given above.

On a Method of Finding the Conductivity for Heat.

By Professor C. NIVEN, F.R.S.

(Received December 5, 1904,—Read January 26, 1905.)

INTRODUCTION.

This paper contains an account of a method for finding the conductivity for heat, especially in bad conductors. The substance is supposed given in the form of a cylinder, or rather of two half-cylinders pressed together and heated by a current passing through a wire along the axis. When the steady state has been reached, the conductivity is given in terms of the difference of temperatures at known distances from the axis, and the heat supplied by the wire. The latter can be found when we know the current passing through it and the difference of potential at its ends.

The first part of the paper contains a detailed account of the methods employed for finding the difference of temperature, and a description of the apparatus used. The results of some experiments made with it are also given, and compared with those found by other observers.

The second part of the paper contains a solution of the mathematical problem of the diffusion of heat in an infinite solid from a line at which it is supplied at a constant rate, and the solution of some other allied questions.

One result of the investigation suggests a method of finding the diffusivity directly, when the substance is of sufficiently great extent.

PART I.

1. If heat be supplied uniformly and continuously to a solid within a given space at the rate of H units per second, and if a surface S be drawn round this space, then when the steady state has been attained and the temperature at each point is constant in time,

$$H = - \int k \frac{d\theta}{dn} dS,$$

the integral being taken over the closed surface, k being the conductivity, and $d\theta/dn$ the normal variation of θ outwards. In particular, if the solid be in the form of a circular cylinder, and the heat be supplied by an electric current passing through a uniform straight wire coinciding with its axis, the equation takes the form

$$H_1 = -k \frac{d\theta}{dr} \cdot 2\pi r,$$

the enclosing surface being a coaxial cylinder, and H_1 the heat supplied per centimetre per second.

If we integrate this equation, we find for the difference of temperatures $\theta_1 - \theta_2$ at distances a, b , from the axis, the expression

$$H_1 \log_e b/a = 2\pi (\theta_1 - \theta_2) k.$$

Upon this equation we may base a method of finding k , since the heat evolved in the wire per unit length is readily found when we know the current i (in ampères) passing through it and its resistance; or what comes to the same thing, the current and the difference of potentials $V_1 - V_2$ (in volts) between two points at a known distance apart. These data can be got by using, say, a Weston millivoltmeter provided with suitable shunts and resistances, and may be obtained with considerable accuracy if the instrument be properly calibrated.

Reducing electrical to heat units the value of the conductivity is given by

$$k = \frac{i(V_1 - V_2) \log_e b/a}{4.2 \times 2\pi (\theta_1 - \theta_2) l},$$

l being the length of the heating wire, at the ends of which the potentials are taken.

The heating wires used were of platinoid. At first wires of No. 40 S.W.G. were used carrying currents of about one ampère, but these were afterwards replaced by thicker wires of No. 34, as they were found to give too great a heating effect, and caused the wood in which they were placed to shrink at the centre, and besides, in addition, were liable to snap when drawn tight. The thicker wires gave more satisfactory results.

2. The temperatures θ_1, θ_2 , or rather $\theta_1 - \theta_2$, were measured either by the change of resistance of platinum wires embedded in the body parallel to the axis, or by thermo-electric junctions formed by soldering together thin iron and German silver wires placed in the same positions as the platinum wires. These fine wires were stretched round two brass pins so as to be at distances about 1 cm. and 3 cm. from the heating wire.

When solids were tested they were made in the form of two half cylinders, one of which was placed in a semi-cylindrical wooden shell, which was moved up till the two wires rested on its flat face. If platinum wires were used their resistances were now compared. The current is then passed through the heating wire, which is drawn tight round a brass pin and fixed to lie parallel to the other two wires.

The second half cylinder and the other semi-cylindrical wooden shell were then placed upon it and squeezed firmly down. If this operation be carefully performed it is possible to fix the wires in their positions, though the thin platinum wires gave some trouble owing to their great fragility.

When the apparatus is used for testing the conductivity of powders, the lower shell is first filled and the wires placed in position on the upper surface of the substance, the current turned on and the heating wire drawn tight. The upper shell is now laid above the first, and filled through a slot made along the top, the powder being distributed to fill it completely.

The apparatus is shown generally in fig. 1. Fig. 2 is a horizontal section

FIG. 1.

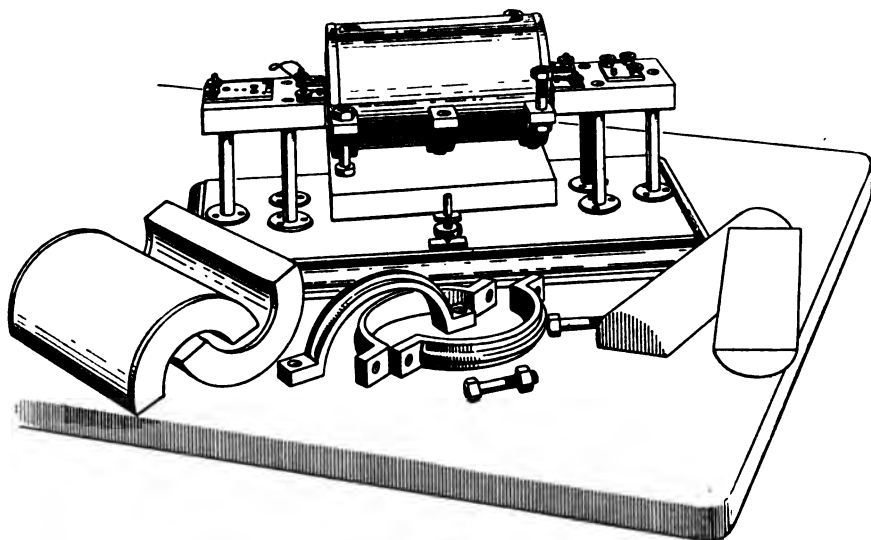
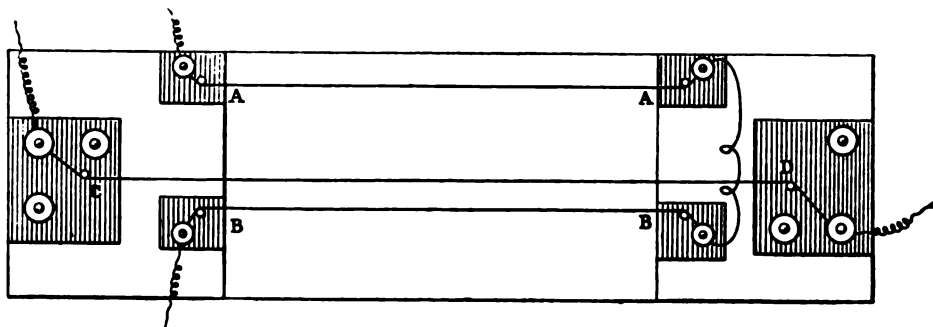


FIG. 2.



in the plane of junction of the two half cylinders; AA, BB are the two thermometric wires, and CD the heating wire fixed to brass plates. The length of the cylinders used was 15 cm., and the diameter 9 cm. The heating wire had a length of 25 cm. in the later experiments.

3. *Thermometric Arrangements.*—(1) When the difference of temperatures

was measured by the change of resistance of platinum, a piece of platinum wire was coated with copper and the whole drawn out till the platinum had a thickness of about 0.035 mm., that of the copper being about 0.27 mm. Any change of resistance was thus appreciably due to the platinum. Two lengths from the same piece were taken, laid together, and being connected with soft wax, were bared as nearly as possible to the same extent of about 3 to 4 cm., so that their resistances were very nearly equal.

If R_0 be the resistance of the inner one, R'_0 that of the outer before heating, let

$$R_0 : R'_0 = \alpha : \beta,$$

when compared by the Wheatstone's Bridge method, taking, say, $\alpha = 1000$ and β a number not far from 1000. After heating, and when the temperature has become steady,

$$R_0 \text{ becomes } R_1 = R_0 [1 + c(\theta_1 - \theta_0)],$$

$$R'_0 \quad \text{,,} \quad R'_1 = R'_0 [1 + c(\theta_2 - \theta_0)],$$

where c is the temperature coefficient of the resistance of platinum, and θ_0 is the temperature of the room.

Suppose now that $R_1 : R'_1 = \alpha : \beta_1$. Then

$$\frac{1 + c(\theta_1 - \theta_0)}{1 + c(\theta_2 - \theta_0)} = \frac{\beta}{\beta_1}.$$

If the total changes of resistance are only comparatively small fractions of the original resistance, we have

$$c(\theta_1 - \theta_2) = (\beta - \beta_1)/\beta_1.$$

Of course, if $c(\theta_2 - \theta_0)$ is a considerable fraction, the resistances must be found separately. In the experiments actually made, $\theta_2 - \theta_0$ amounted to about 30° at most, and $c = 1/400$, so that the assumption here made is sufficiently accurate.

(2) So much difficulty was experienced in the use of these fine platinum wires, especially in testing loose powders such as sand or mould, that they were ultimately given up, and the difference of temperatures found by the thermo-electric junctions already described. The arrangement used was a wire of German silver of 0.2 mm. diameter between two iron wires of the same diameter, stretched parallel to the axis of the cylinder so that the two wires, and, therefore, the junctions, were at the distances apart previously chosen, that is to say, 1 cm. and 3 cm. from the heating wire. As the resistance of the galvanometer employed was about 800 ohms, the deflection

was sensibly proportional to the difference of temperature. By independent experiments one scale division represented 0.70°C .

4. With regard to the choice of the distances a, b from the central wire, it is clear that these should not be taken too nearly equal; for, unless b be a moderate multiple of a , any error in the measurement of one of them, say a , will introduce a large error in $\log_e b/a$.

$$\begin{aligned} \text{Let} \quad a' \text{ for instance} &= a(1 - 1/n), \\ \log_e b/a' &= \log b/a + 1/n, \text{ nearly.} \end{aligned}$$

Thus, if $a = 1 \text{ cm.}$, $b = 1.5 \text{ cm.}$, and $\frac{1}{n}a = 0.5 \text{ mm.}$,

$$\log b/a = 0.405, \quad 1/n = 0.05,$$

so that the error is about 12 per cent. of the whole.

By taking $b/a = 3$ the error lies between 4 and 5 per cent.

As between the two pairs of distances 1, 6 and 2, 6 cm., we should rather choose the latter, as $\log_e 6$ is not quite $2 \log_e 3$, and an error of 0.5 mm. in 2 cm. is only half as important as the same error in 1 cm.

In the present form of the apparatus I have therefore taken $a = 1 \text{ cm.}$, $b = 3 \text{ cm.}$; and in a larger model, $a = 2 \text{ cm.}$, $b = 6 \text{ cm.}$

5. It is desirable to know how long an experiment need be continued to get a fair approximation to the steady state. For this purpose it is necessary to know how the temperature rises at any point.

In the second part of this paper the solution is given of the problem of the diffusion of heat in an infinite cylinder from a steady source at the axis. Taking the result as a guide for the present case, we have

$$\theta_1 - \theta_2 = \frac{a}{2} \int_{a/\sqrt{nt}}^{b/\sqrt{nt}} x^{-1} e^{-x^2/4} dx,$$

where $x^2 = r^2/nt$, and r is the distance from the axis and n the diffusivity.

Assuming, provisionally, that $r^2/4nt$ is large enough to make $r^2/4nt$ small, we may expand $e^{-r^2/4nt}$, and retain only the first two terms. Thus

$$\theta_1 - \theta_2 = a \left(\log \frac{b}{a} - \frac{b^2 - a^2}{8nt} \right).$$

The first term of the expression gives the temperature of the steady state, and if the temperature be 5 per cent. below its final value,

$$\frac{b^2 - a^2}{8nt} = \frac{1}{20} \log_e \frac{b}{a}.$$

If $a = 1 \text{ cm.}$, $b = 3 \text{ cm.}$,

$$t = 18.2/n.$$

In the case of sand, for which n is given, 0.0032 (Everett's 'Units and Physical Constants')

$$t = 5702, \text{ or about } 1\frac{1}{2} \text{ hours.}$$

To get within 1 per cent., we should have to continue the heating for about $7\frac{1}{2}$ hours.

It may, perhaps, be worth remarking that the diffusivity may be found directly from the expression for $d\theta/dt$ given in the second part of the paper and quoted above; for

$$\frac{d\theta}{dt} = \frac{a}{t} e^{-r^2/4nt},$$

which is a maximum when

$$t = r^2/4n.$$

Taking $r = 3$ cm., the time required is only about one-eighth of that previously necessary.

6. As an illustration of the results which the method gives, I add a list of some substances whose conductivities have been found by it. In the case of the woods, the flow of heat is across the fibres. In the second column the letter R indicates that the difference of temperatures was found by the change of resistance of the platinum wires, J that it was found by thermo-electric junctions. The distances of the thermometric wires from the central wires are given in the third and fourth columns; in the earlier experiments, b/a was taken nearly = 1.5, while in the later ones b/a is about 3. The numbers agree fairly well, though, for the reasons given above, I think the latter ratio preferable. The fifth column shows the size of the platinoid wire used as the source of heat, and the sixth the current passing through it.

Some determinations by other observers are added; these are taken from Everett's 'Units and Physical Constants.'

I wish to express my indebtedness to Mr. William Mitchell, M.A., by whom many of these determinations were made, for this and other assistance he has given me in the course of the work.

Substance.	Thermo- metric means.	Distances from the central wire.		No. of wire S.W.G.	Currents in amperes.	Conduc- tivity $\times 10^4$.	Authority.
		a.	b.				
Fir	R R R	1.19 0.9 0.9	1.57 1.4 3.07	34 40 40	0.83 0.87 0.9	2.64 3.94 2.95	G. Forbes. Peclet.
Butternut	R	1.0	1.5	34	0.86	2.97	
Mahogany	R	1.09	1.53	40	0.61	3.66	
	J	1.05	2.91	34	1.22	3.06	B.A. Committee. (Ordinary) Peclet. (Fine) Peclet.
	R	1.0	1.5	40	0.87	4.58	
Beech	J	1.01	2.9	34	1.22	3.67	
	R	0.97	1.38	40	0.89	3.7	
Plaster-of-Paris (made-up)	R	0.85	1.4	40	0.87	10.7 12.0	
Sand (fine)	R	1.2	2.3	40	0.85	6.52	G. Forbes. B.A. Committee. Peclet.
	J	0.96	2.9	34	1.25	6.08	
	J	1.0	2.8	34	1.04	7.10 1.31	
Garden mould (dry)	J	0.92	2.9	34	1.25	4.80	G. Forbes. (Mahogany) Peclet.
Sawdust (fir)	J	0.97	2.87	34	1.23	1.72	
"	—	—	—	—	—	1.23	
"	—	—	—	—	—	1.8	

PART II.

In connection with the foregoing method, based on the steady state, it seemed desirable to know the mode in which this state is attained at any time after the heating is begun. As a preliminary, the problem of the heating of a rod by heat supplied uniformly in the middle, was first attacked in Fourier's way by treating it as the limit of a ring of infinite radius. The results, though complicated in form, may be worth recording, as the conditions approximate to those actually met with when one end of a metal rod is put into a hot flame.

The case of a small spherical cavity is added, and may be taken as an illustration of the way in which the heat given out by a small morsel of radium is propagated through an infinite solid.

In all the questions treated in this part the body is supposed infinite in the directions in which the flow of heat is considered, the ring and thin spherical shell excepted.

CASE 1. Thin Circular Ring with Surface Impermeable to Heat.—Consider first the case of a uniform thin circular ring heated at one spot.

Let k = conductivity, σ = specific heat per unit volume,
 A = cross-section of ring, c = its mean radius,
 s = an arc of ring measured from the heated spot,
 ϕ = the angle subtended by s at the centre, so that $s = c\phi$,
 H = heat supplied at the spot per second.

The general equation of conduction is

$$kA \frac{d^2\theta}{ds^2} = A\sigma \frac{d\theta}{dt}, \quad \text{or} \quad \frac{k}{c^2} \frac{d^2\theta}{d\phi^2} = \sigma \frac{d\theta}{dt} \dots\dots\dots (1),$$

θ being the temperature.

If the heat has been supplied for a long time t , the temperature will be sensibly uniform throughout and equal to

$$Ht/2\pi cA\sigma.$$

If we include the effect of conduction we may satisfy Equation (1) by adding to this a term of the form $B\phi^3 + C\phi + D$, where

$$B = Hc/2\pi Ak$$

and the other constants are undetermined.

To complete the general solution we have to add terms of the form

$$L + \sum M_i \cos i\phi e^{-\lambda_i t} \dots\dots\dots (2),$$

where

$$\lambda_i = k i^2 / c^2 \dots\dots\dots (3).$$

We have also to satisfy the conditions that the flow of heat outwards at the origin O is constantly equal to $\frac{1}{2}H$ on either side, that is, corresponding to $\phi = 0, \phi = 2\pi$.

All these conditions are satisfied by the expression

$$\theta = \frac{Ht}{2\pi cA\sigma} + \frac{Hc}{2\pi Ak} (\phi - \pi)^2 + L + \sum M_i \cos i\phi e^{-\lambda_i t} \dots\dots (4).$$

It will be noted that the last terms give no flow at O, on either side, nor at the diametrically opposite point, as ought, from symmetry to be the case.

The constants L, M are determined in the usual way by taking $\theta = 0$, when $t = 0$, all over the ring. Thus

$$L \int_0^{2\pi} d\phi + \frac{Hc}{2\pi Ak} \int_0^{2\pi} (\phi - \pi)^2 d\phi = 0;$$

$$M_i \int_0^{2\pi} \cos^2 i\phi d\phi + \frac{Hc}{2\pi Ak} \int_0^{2\pi} (\phi - \pi)^2 \cos i\phi d\phi = 0.$$

And, finally,

$$\theta = \frac{Ht}{2\pi cA\sigma} + \frac{Hc(\phi - \pi)^2}{4\pi Ak} - \frac{\pi Hc}{12Ak} - \frac{Hc}{\pi Ak} \sum_1 \frac{1}{i^2} \cos i\phi e^{-\lambda_i t} \dots\dots (5).$$

CASE 2. *Infinite Straight Rod Heated at the Middle.*—By putting

$$c\phi = x, \quad i/c = z, \quad 1/c = \partial z, \quad \text{and } c = \infty,$$

we pass, in Fourier's way, to the case of an infinite straight rod.

$$\theta = -\frac{Hx}{2\pi Ak} + \frac{Hc\pi^2}{6\pi Ak} - \frac{H}{\pi Ak} \int_0^\infty \frac{1}{z^2} \cos zx e^{-kt^2/\sigma} dz.$$

The second term, which is infinite, may be treated thus—

$$\pi^2/6 = 1/1^2 + 1/2^2 + 1/3^2 + \dots$$

$$c\pi^2/6 = \frac{1}{c} \sum c^2/z^2 = \int_0^\infty z^{-2} dz.$$

If we integrate the last term by parts, dropping the factor $H/\pi Ak$ and include this term, we have

$$\left[-\frac{1}{z} + \frac{1}{z} \cos zx e^{-kt^2/\sigma} \right]_0^\infty + \int_0^\infty \frac{x \sin zx}{z} e^{-kt^2/\sigma} dz + \frac{2kt}{\sigma} \int_0^\infty \cos zx e^{-kt^2/\sigma} dz,$$

and the part outside the integral sign now vanishes at both limits.

If we put $n = k/\sigma$,

$$\int_0^\infty \cos zx e^{-nt^2} dz = \frac{\pi}{2\sqrt{nt}} \times e^{-x^2/4nt},$$

$$\int_0^{\infty} \frac{\sin zx}{z} e^{-nt^2} dz = \frac{\pi}{2\sqrt{nt}} \int_0^x e^{-x^2/4nt} dx,$$

and thus finally

$$\theta = -\frac{Hx}{2Ak} + \frac{H}{\pi Ak} \left\{ 2nte^{-x^2/4nt} + x \int_0^x e^{-x^2/4nt} dx \right\} \frac{\pi}{2\sqrt{nt}} \dots\dots\dots (6).$$

CASE 3. *Ring with Radiating Surface.*—If P be the perimeter of a cross section, and h the constant of radiation, the equation of the flow of heat along the ring is

$$\frac{kA}{c^2} \frac{d^2\theta}{d\phi^2} = A\sigma \frac{d\theta}{dt} + Ph\theta \dots\dots\dots (7).$$

If the flow of heat from the source were continued for a long time t , the final temperature, neglecting conduction, would be given by

$$\theta = \frac{H}{2\pi chP} (1 - e^{-\lambda P\theta/A\sigma}).$$

Including conduction, it is easy to see that the general Equation (7) is satisfied by an expression of the form

$$\theta = -\frac{H}{2\pi chP} e^{-\lambda P\theta/A\sigma} + B(e^{m(\phi-\pi)} + e^{-m(\phi-\pi)}) + L + \sum M_i \cos i\phi e^{-\lambda t} \dots (8),$$

where

$$\left. \begin{aligned} m^2/c^2 &= Ph/Ak, \\ \lambda \cdot A\sigma &= kAi^2/c^2 + Ph \end{aligned} \right\} \dots\dots\dots (9).$$

The condition that the flow at either side of the origin should be equal to $H/2$ requires that

$$-B \cdot m/c \cdot kA (e^{-m\pi} - e^{m\pi}) = H/2,$$

when $t = 0$, $\theta = 0$ everywhere.

Thus

$$L - \frac{H}{2\pi chP} + B(e^{m(\phi-\pi)} + e^{-m(\phi-\pi)}) + \sum M_i \cos i\phi = 0.$$

Determining the constants L , M_i in the usual way,

$$L = 0, \quad M_i = -\frac{H}{\pi Ak} \frac{c}{i^2 + m^2}.$$

Thus, finally,

$$\theta = \frac{H}{2\pi chP} e^{-\lambda P\theta/A\sigma} + \frac{H}{2} \frac{c}{m Ak} \frac{e^{m(\phi-\pi)} + e^{-m(\phi-\pi)}}{e^{m\pi} - e^{-m\pi}} - e^{-\lambda P\theta/A\sigma} \frac{Hc}{\pi Ak} \sum \frac{\cos i\phi}{i^2 + m^2} e^{-i^2 t/c^2} \dots\dots\dots (10).$$

CASE 4. *Infinite Radiating Rod.*—To pass to this case, put $c\phi = x$, $c = \infty$. If then $p^2 = Ph/Ak$, $m = cp$, and $\frac{e^{m(\phi-\pi)} + e^{-m(\phi-\pi)}}{e^{m\pi} - e^{-m\pi}} = \frac{e^{-px} + e^{px}e^{-2c\pi}}{1 - e^{-2c\pi}} = e^{-px}$,

$$\theta = \frac{H}{2Ak} \frac{e^{-px}}{p} - \frac{H}{\pi Ak} e^{-Ph/A\sigma} \int_0^\infty \frac{\cos zx}{z^2 + p^2} e^{-\pi iz^2} dz \dots\dots\dots (11).$$

This integral may be expressed in terms of two integrals of the error-function type, but it is unnecessary to give the reduction here.

CASE 5. *Thin Spherical Shell.*—The case of an infinite cylinder heated from a wire passing along its axis is the same as the two-dimensional problem of a plate heated at a point.

To treat this, consider first the case of a thin spherical shell, heated steadily from a small circular hole, and take the boundary of the shell to be impermeable to heat.

The general equation of the flow along the shell is

$$\frac{k}{a^2} \frac{d}{d\mu} \left\{ (1-\mu^2) \frac{d\theta}{d\mu} \right\} = \sigma \frac{d\theta}{dt} \dots\dots\dots (12),$$

a being the radius of the shell, $\mu = \cos \vartheta$, ϑ = angular distance from hole.

If e be its thickness, the final state, after a long time t , is given by

$$\theta_f = \frac{Ht}{4\pi a^2 e \sigma}.$$

To satisfy Equation (12) generally, including this term, we require a term q such that

$$k \frac{d}{d\mu} \left\{ (1-\mu^2) \frac{dq}{d\mu} \right\} = \frac{H}{4\pi e},$$

whence $(1-\mu^2) \frac{dq}{d\mu} = \alpha (\mu + C)$, where $\alpha = \frac{H}{4\pi ek}$.

And the complete value of θ will be

$$\theta_f + q + \sum_0^\infty M_i P_i e^{-\lambda_i t},$$

where $\lambda = i(i+1)k/a^2\sigma$, P_i being the usual zonal harmonic of degree i .

The flow across any small circle ϑ is

$$-ke \times 2\pi a \sin \vartheta \frac{d\theta}{a d\vartheta} = 2\pi ke (1-\mu^2) \frac{d\theta}{d\mu}.$$

The part of this depending on P_i vanishes when $\vartheta = 0$ or $\mu = 1$; and, if $C = 1$, the part derived from q will be equal to H . Thus

$$\frac{dq}{d\mu} = \frac{\alpha}{(1-\mu)}, \quad \text{or} \quad q = -\frac{H}{4\pi ek} \log(1-\mu).$$

The complete expression for θ is therefore

$$\frac{Ht}{4\pi a^2 c \sigma} - \frac{H}{4\pi e k} \log(1-\mu) + \sum_0 M_i P_i e^{-\lambda t} \dots \dots \dots (13).$$

To determine M_i we have, when $t = 0$,

$$M_i \int_{-1}^{+1} P_i^2 d\mu + \int_{-1}^{+1} q P_i d\mu = 0.$$

Now
$$\frac{d}{d\mu} \left\{ (1-\mu^2) \frac{dP_i}{d\mu} \right\} = -i(i+1) P_i,$$

and
$$\frac{d}{d\mu} \left\{ (1-\mu^2) \frac{dq}{d\mu} \right\} = a.$$

Hence

$$\int_{-1}^{+1} a P_i d\mu + i(i+1) \int_{-1}^{+1} P_i q d\mu = \left\{ (1-\mu^2) \left(P_i \frac{dq}{d\mu} - q \frac{dP_i}{d\mu} \right) \right\}_{-1}^{+1}.$$

The first term on the left hand vanishes except when $i = 0$. On the right hand $(1-\mu^2) \frac{dq}{d\mu} P_i = a(1+\mu) P_i = 2a$, between the limits; and

$$(1-\mu^2) q \frac{dP_i}{d\mu} = (1-\mu) \log(1-\mu) \times (1+\mu) \frac{dP_i}{d\mu},$$

which vanishes both when $\mu = 1$ and when $\mu = -1$. Thus

$$M_i = -a(2i+1)/i(i+1).$$

The constant term M_0 is given from

$$\begin{aligned} M_0 \int_{-1}^{+1} d\mu &= a \int_{-1}^{+1} \log(1-\mu) d\mu = -a \{ (1-\mu) \log(1-\mu) - (1-\mu) \} \Big|_{-1}^{+1} \\ &= a(2 \log 2 - 2), \end{aligned}$$

or $M_0 = a(\log 2 - 1).$

Thus the complete expression for θ is

$$\theta = \frac{Ht}{4\pi a^2 c \sigma} - a \left\{ \log \left(\frac{1-\mu}{2} \right) + 1 \right\} - a \sum_1^{\infty} \frac{2i+1}{i(i+1)} P_i e^{-\lambda t} \dots \dots \dots (14)$$

where

$$a = H/4\pi e k.$$

When $t = 0$, $\theta = 0$ everywhere, and this requires that

$$\log \frac{1-\mu}{2} + 1 + \sum \frac{2i+1}{i(i+1)} P_i = 0,$$

an expression which may be readily verified from the expression

$$(1-2\mu x + x^2)^{-1} = 1 + \sum P_i x^i.$$

CASE 6.—*Infinite Plane Plate.* This case, which also includes that of an infinite cylinder heated along its axis, may be deduced from the foregoing one by putting

$$1 - \mu = 2 \left(\frac{r}{2a} \right)^2,$$

r being the distance of any point from the centre, and by taking

$$i/a = z, \quad 1/a = \partial z, \quad \lambda = kx^2/\sigma;$$

also

$$P_i = J_0(zr),$$

and the expression for θ is

$$\theta = -\frac{H_1}{4\pi k} \left(2 \log \frac{r}{2} + 1 \right) + \frac{H_1}{2\pi k} \left[\log a - \int_0^\infty z^{-1} J_0(rz) e^{-nz^2} dz \right] \dots \quad (15),$$

where H_1 stands for the heat supplied per unit length in unit time, and $n = k/\sigma$.

The integral, which itself is infinite, is coupled with an infinite term, the difference between the two being the finite part on which the solution depends. The same point came up in the deduction of the solution for the infinite rod from that of the ring, but in that case it was possible to assign a finite form for the difference.

The form of the integral in (15) suggests, as will be seen later, another way of obtaining the solution, but it is possible to deduce from it a form of solution satisfying all the conditions of the problem. For if we differentiate the above expression with regard to the time, we have

$$\frac{d\theta}{dt} = \frac{H_1}{2\pi k} n \int_0^\infty z J_0(rz) e^{-nz^2} dz;$$

or, putting

$$\zeta = z\sqrt{nt}, \quad x = r/\sqrt{nt},$$

we have

$$\frac{d\theta}{dt} = \frac{H_1}{4\pi k t} u, \quad u = \int_0^\infty \zeta J_0(x\zeta) e^{-\zeta^2} d\zeta.$$

It is easy to verify by direct differentiation that

$$2 \frac{du}{dx} + ux = 0,$$

and therefore

$$u = Ae^{-x^2/4}.$$

To find the constant A , we observe that when

$$x = 0, \quad u = \int_0^\infty \zeta e^{-\zeta^2} d\zeta = \frac{1}{2}; \quad \text{so that } A = \frac{1}{2}$$

Thus

$$\frac{d\theta}{dt} = \frac{H_1}{4\pi k t} e^{-x^2/4}, \quad \theta = \frac{H_1}{4\pi k} \int_0^t t^{-1} e^{-x^2/4} dt.$$

But

$$x^2 = r^2/nt, \text{ and therefore } 2dx/x + dt/t = 0.$$

Thus

$$\theta = \frac{H_1}{2\pi k} \int_0^\infty x^{-1} e^{-x^2/4} dx. \dots\dots\dots (16).$$

Another Solution of this Case.—The expression just given for θ was originally obtained by a different method, which may be now given. The integral contained in the Equation (15), viz.,

$$\int_0^\infty x^{-1} J_0(rx) e^{-nx^2} dx,$$

may be written, using the same symbol ζ , as above, in the form

$$\int_0^\infty \zeta^{-1} J_0(\zeta r / \sqrt{nt}) e^{-\zeta^2} d\zeta,$$

which shows that θ is of the form $\phi(r^2/nt)$.

But the general equation of the flow of heat in two dimensions is

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} = \frac{1}{n} \frac{d\theta}{dt},$$

which may be satisfied by $\theta = \phi(v)$, where $v = (x^2 + y^2)/nt$, if

$$4 \frac{d\phi}{dv} + 4v \frac{d^2 \phi}{dv^2} = -v \frac{d\phi}{dv},$$

and therefore

$$v \frac{d\phi}{dv} = A e^{-v/4}.$$

The total flow across the boundary of the circle of radius, r , in unit time

$$= -2\pi r k \frac{d\theta}{dr} = -4\pi k v \frac{d\phi}{dv},$$

and when $r = 0$, or $v = 0$, this is to be equal to H_1 . Therefore

$$A = -H_1/4\pi k.$$

Thus

$$\theta = \frac{H_1}{4\pi k} \int_0^\infty v^{-1} e^{-v/4} dv,$$

the upper limit of integration being taken to make θ everywhere = 0, when $t = 0$

Writing x^2 for v , this expression becomes the same as that previously found in Equation (16).

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CASE 7. Case of an Infinite Solid with small Spherical Source.—The equation of motion in this case is

$$k \left(\frac{d^2 \theta}{dr^2} + \frac{2}{r} \frac{d\theta}{dr} \right) = \sigma \frac{d\theta}{dt},$$

or
$$n \frac{d^2(\theta r)}{dr^2} = \frac{d(\theta r)}{dt} \dots\dots\dots (17),$$

where $n = k/\sigma.$

When t is infinite and the flow has become steady,

$$\theta = A/r + B, \text{ where } k \cdot 4\pi A = H.$$

But the general Equation (17) is satisfied also by

$$\theta r = \int_0^\infty \phi(z) \cos zr e^{-nt^2} dz, \text{ and by } \int_0^\infty \phi(z) \sin zr e^{-nt^2} dz.$$

If we choose the latter, and put $\phi(z) = C/z$, we may take as the solution applicable to the present case

$$\theta = \frac{H}{4\pi k r} + \frac{C}{r} \int_0^\infty \frac{\sin zr}{z} e^{-nt^2} dz.$$

For,

(1) When $t = \infty$, it reproduces the steady state;

(2) When $t = 0$, $\theta = \frac{1}{r} \left(\frac{H}{4\pi k} + C \int_0^\infty \frac{\sin zr}{z} dz \right),$

$$= \frac{1}{r} \left(\frac{H}{4\pi k} + \frac{\pi}{2} C \right),$$

which vanishes if

$$C = -2/\pi \cdot H/4\pi k;$$

$$(3) \quad -4\pi k r^2 \frac{d\theta}{dr} = H - \frac{2H}{\pi} \int_0^\infty \frac{\sin zr}{z} e^{-nt^2} dz + \frac{2Hr}{\pi} \int_0^\infty \cos zr e^{-nt^2} dz,$$

which is equal to H when $r = 0$. All the conditions are therefore satisfied.

The solution therefore is

$$\theta = \frac{H}{4\pi k r} \left(1 - \frac{2}{\pi} \int_0^\infty \frac{\sin zr}{z} e^{-nt^2} dz \right) = \frac{H}{4\pi k r} \left(1 - \frac{1}{\sqrt{nt}} \int_0^r e^{-r^2/4nt} dr \right).$$

Theory of the Reflection of Light near the Polarising Angle.

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Supposing the phenomena of light to be due to displacements in a rotational ether, we have the following expressions for the kinetic energy and work function in a transparent isotropic medium:—

$$T = \frac{1}{2} \int \rho (\xi^2 + \eta^2 + \zeta^2) dV,$$

$$W = \frac{1}{2} c^2 \int \rho \mu^2 (f^2 + g^2 + h^2) dV.$$

Here dV denotes an element of volume, ρ is the density, $\xi\eta\zeta$ the displacement, $(fgh) = \frac{1}{\mu^2} \text{curl} (\xi\eta\zeta)$, c a constant that will prove to be the velocity of light in free ether, whereas μ will be identified with the refractive index.

The dynamical equations and boundary conditions are most simply obtained from the Principle of Action, which makes

$$\delta \int (T - W) dt = 0.$$

We have
$$\delta \int (T - W) dt = \Sigma \int \int \rho (\xi \delta \xi - c^2 \mu^2 f \delta f) dt dV,$$

$$\int \xi \delta \xi dt = \xi \delta \xi - \int \xi \delta \xi dt.$$

The term containing $\delta \xi$ in the variation of δW is

$$c^2 \int \rho \left(g \frac{\partial \delta \xi}{\partial z} - h \frac{\partial \delta \xi}{\partial y} \right) dV = c^2 \int \rho (ng - mh) \delta \xi dS - c^2 \int \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right) \delta \xi dV,$$

where (l, m, n) are the direction cosines of the outward normal to the bounding surface S .

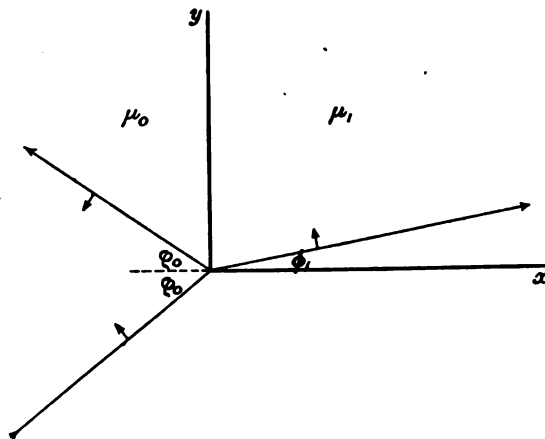
Picking out the coefficient of $\delta \xi$ in the variation, we get

$$\xi = c^2 \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right), \quad (i)$$

and the surface conditions require $\rho c^2 (ng - mh)$, $\rho c^2 (lh - nf)$, $\rho c^2 (mf - lg)$, to be continuous. The displacement $(\xi\eta\zeta)$ must also be continuous to avoid

rupture of the medium. We shall take ρ to be continuous, and if the surface of separation between different media be $x = \text{constant}$, the boundary conditions are satisfied when g, h, ξ, η, ζ are continuous. These boundary conditions combined with three dynamical equations of the type (i) will suffice to solve completely the problem of the reflection and refraction of light at the boundary of two transparent isotropic media. We take (f, g, h) to represent the light vector, and if we wish to interpret results in the language of electric theory, we identify (f, g, h) with the electric displacement, and take ξ, η, ζ proportional to the magnetic force.

We shall first consider the case of an abrupt transition from one medium to the other. The surface of separation is $x = 0$, the plane of xy is that of incidence, so that everything is independent of z .



(1) Vibrations (of f, g, h) *parallel* to the plane of incidence; so that (ξ, η, ζ) is at right angles to this plane.

Thus $\xi = 0 = \eta$;

$$\zeta_0 = e^{ipt - i(x \cos \phi_0 + y \sin \phi_0)/V_0} \text{ (incident)}$$

$$+ r e^{ipt - i(x \cos \phi' + y \sin \phi')/V_0} \text{ (reflected);}$$

$$\zeta_1 = \frac{\mu_1}{\mu_0} \cdot s e^{ipt - i(x \cos \phi_1 + y \sin \phi_1)/V_1} \text{ (refracted).}$$

The boundary conditions require the exponential factor to be the same for all values of t and y when $x = 0$; thus

$$\sin \phi_0/V_0 = \sin \phi'/V_0 = \sin \phi_1/V_1,$$

whence $\phi' = 180^\circ - \phi_0$, which is the law of reflection; and $\sin \phi_0/V_0 = \sin \phi_1/V_1$,

which is the law of refraction for $V = c/\mu$ in order that the dynamical equation (i) for S may be satisfied.

$$f = \frac{1}{\mu^2} \frac{\partial S}{\partial y}; \quad g = -\frac{1}{\mu^2} \frac{\partial S}{\partial x}; \quad h = 0.$$

Thus

$$f_0 = -\frac{ip}{c\mu_0} \sin \phi_0 [e^{ip(\dots)} + r e^{ip(\dots)}]; \quad f_1 = -\frac{ip}{c\mu_0} \sin \phi_1 [s e^{ip(\dots)}];$$

$$g_0 = -\frac{ip}{c\mu_0} \cos \phi_0 [e^{ip(\dots)} - r e^{ip(\dots)}]; \quad g_1 = \frac{ip}{c\mu_0} \cos \phi_1 [s e^{ip(\dots)}].$$

These represent waves (of f, g, h) whose amplitudes are in the ratios $1:r:s$.

The boundary conditions give $1+r = \mu_1/\mu_0 \cdot s$; $\cos \phi_0 (1-r) = s \cos \phi_1$; whence, remembering that $\mu_0 \sin \phi_0 = \mu_1 \sin \phi_1$, we get

$$r = \frac{\tan(\phi_0 - \phi_1)}{\tan(\phi_0 + \phi_1)} \quad \text{and} \quad s = \frac{2 \sin \phi_1 \cos \phi_0}{\sin(\phi_0 + \phi_1) \cos(\phi_0 - \phi_1)}.$$

2. Vibrations (of f, g, h) *perpendicular* to the plane of incidence. In this case it is convenient to introduce a new vector (ξ', η', ζ') , of which (ξ, η, ζ) is the curl.

$$\xi' = 0 = \eta'; \quad \xi = \frac{\partial \xi'}{\partial y}; \quad \eta = -\frac{\partial \xi'}{\partial x}; \quad \zeta = 0.$$

$$f = 0; \quad g = 0; \quad h = -\frac{1}{\mu^2} \nabla^2 \xi'.$$

Take $\xi'_0 = e^{ipt - i(x \cos \phi_0 + y \sin \phi_0)/V_0} + r' e^{ipt + i(x \cos \phi_0 - y \sin \phi_0)/V_0}$

$$\xi'_1 = s' e^{ipt - i(x \cos \phi_1 + y \sin \phi_1)/V_1}.$$

Then the amplitude of the incident, reflected, and refracted waves (of f, g, h) are in the ratios $1:r':s'$.

$$\xi_0 = -\frac{ip}{c} \mu_0 \sin \phi_0 [e^{ip(\dots)} + r' e^{ip(\dots)}]; \quad \xi_1 = -\frac{ip}{c} \mu_1 \sin \phi_1 [s' e^{ip(\dots)}];$$

$$\eta_0 = \frac{ip}{c} \mu_0 \cos \phi_0 [e^{ip(\dots)} - r' e^{ip(\dots)}]; \quad \eta_1 = \frac{ip}{c} \mu_1 \cos \phi_1 [s' e^{ip(\dots)}].$$

The boundary conditions give $1+r'=s'$; $\mu_0 \cos \phi_0 (1-r') = \mu_1 \cos \phi_1 s'$, whence

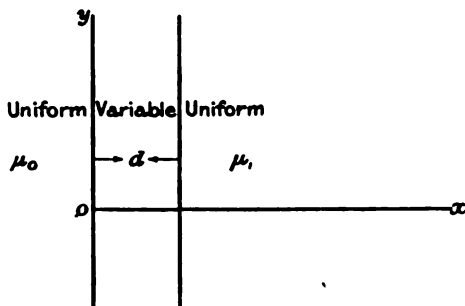
$$r' = -\frac{\sin(\phi_0 - \phi_1)}{\sin(\phi_0 + \phi_1)} \quad \text{and} \quad s' = \frac{2 \sin \phi_1 \cos \phi_0}{\sin(\phi_0 + \phi_1)}.$$

If the incident light is plane polarised at an azimuth of 45° to the plane of incidence, then the amplitudes of the incident light are equal for the vibrations parallel and perpendicular to the plane of incidence. After reflection and refraction the amplitudes will no longer be equal. Let ϵ_1 be the ratio of

the amplitude of the reflected light polarised parallel to the plane of incidence to that polarised at right angles, and let ϵ_2 be the same ratio for the refracted light. Then ϵ_1 and ϵ_2 are the "coefficients of ellipticity" of the reflected and refracted light, and we have :—

$$\epsilon_1 = \frac{r}{r'} = -\frac{\cos(\phi_0 + \phi_1)}{\cos(\phi_0 - \phi_1)} \quad \text{and} \quad \epsilon_2 = \frac{1}{\cos(\phi_0 - \phi_1)}.$$

The formulæ for r and r' agree with those of Fresnel. They make ϵ_1 vanish when $\theta_0 + \theta_1 = 0$, i.e., when $\theta_0 = \tan^{-1} \mu_1 / \mu_0$ the polarising angle; and they indicate a sudden change of phase of 180° (half a wave-length) at this angle. Experiments show that these formulæ represent the facts very well as far as the ellipticity is concerned, except in the neighbourhood of the polarising angle. It is found, however, that ϵ_1 is sensible at all angles, although smallest at the Brewsterian angle, and that the change of phase does not occur suddenly, but enters by degrees. The explanation of this departure from Fresnel's formulæ was long ago ascribed to a gradual rather than an abrupt transition from one medium to the other. This suggestion was strongly supported by Rayleigh's experiment on reflection from water having its surface artificially cleansed, and by the observation made in 1899 by Drude that the ellipticity of the polarisation of the reflected light in the case of a freshly split surface of rock salt is very small, but that it rapidly increases on standing. It seems probable that Fresnel's formulæ are rigorously applicable to the ideal case of an abrupt transition between two isotropic transparent media, and that the departure from these formulæ is due to the fact that in most experiments there is what has been called a "layer of transition" between the media. The mathematical treatment of the problem of the layer has been undertaken by various writers—amongst others Lorenz, Van Ryn,



Van Alkemaade, and Drude on the Continent, and in England, in an illustrative way, by Lord Rayleigh, and systematically by G. A. Schott.* Schott's

* 'Phil. Trans.,' A, 1894, pp. 823 to 885.

analysis is long and complicated, and leads him to results which do not colligate the experimental facts any more closely than very much simpler formulæ that can be obtained. Drude's investigation* is more direct, but from a mathematical point of view his analysis leaves something to be desired, since he treats certain quantities as "approximately constant" merely because they are continuous, and, further, because in proceeding by approximation he gives no indication of the magnitude of the terms neglected.

Take the variable "layer of transition" to extend from $x = 0$ to $x = d$ and to be continuous (as regards μ) with the media bounding. In the layer μ is a function of x only. It will be convenient to put $\mu_0 \sin \phi_0 = \mu_1 \sin \phi_1 = \nu$,

$$\mu_0 \cos \phi_0 = \kappa_0, \quad \mu_1 \cos \phi_1 = \kappa_1.$$

(1) Vibrations *parallel* to the plane of incidence (cf. p. 50).—

In the layer $\zeta = ue^{ip(t-\nu y/c)}$ where u is a function of x only,

$$f = \frac{1}{\mu^2} \frac{\partial \zeta}{\partial y} = \frac{ip\nu}{c\mu^2} ue^{ip(t-\nu y/c)},$$

$$g = -\frac{1}{\mu^2} \frac{\partial \zeta}{\partial x} = -\frac{1}{\mu^2} \frac{du}{dx} e^{ip(t-\nu y/c)}.$$

The equation for S (see (i), p. 49) is $\ddot{\zeta} = c^2 \left(\frac{\partial^2 f}{\partial y^2} - \frac{\partial^2 g}{\partial x^2} \right)$.

Thus

$$-p^2 u = c^2 \left[-\frac{p^2 \nu^2}{c^2 \mu^2} u + \frac{d}{dx} \left(\frac{1}{\mu^2} \frac{du}{dx} \right) \right],$$

i.e.,

$$\frac{d}{dx} \left(\frac{1}{\mu^2} \frac{du}{dx} \right) + \frac{p^2}{c^2} \left(1 - \frac{\nu^2}{\mu^2} \right) u = 0.$$

Put $x/d = x_1$ and $d_1 = pd/c = 2\pi d/\lambda_0 \mu_0 = 2\pi d/\lambda_1 \mu_1$, and we get

$$\frac{d}{dx_1} \left(\frac{1}{\mu^2} \frac{du}{dx_1} \right) + d_1^2 \left(1 - \frac{\nu^2}{\mu^2} \right) u = 0. \quad (\text{ii})$$

This equation, of course, cannot be solved completely until we know μ^2 as a function of x (and therefore of x_1), i.e., until we know the law of variation of μ in the layer. However, in all cases to which we shall apply the solution, d_1 is a small quantity (as will be shown later), and we can thus solve (ii) by approximations.† We get a first approximation by neglecting d_1^2 , so that (ii) becomes

$$\frac{d}{dx_1} \left(\frac{1}{\mu^2} \frac{du}{dx_1} \right) = 0, \quad \text{whence} \quad \frac{1}{\mu^2} \frac{du}{dx_1} = B,$$

and

$$u = A + B \int_0^{x_1} \mu^2 dx_1 = A + B\mu^2 M,$$

where M is a function of x_1 .

* "Lehrbuch der Optik," Transl. Mann and Millikan, p. 288.

† [A somewhat similar analysis has been employed by L. Lorenz.—Sec.]

As a next approximation, put $u = A + B\mu^2 M + d_1^2 v$, and the equation for v is

$$\frac{d}{dx} \left(\frac{1}{\mu^3} \frac{dv}{dx_1} \right) + \left(1 - \frac{v^2}{\mu^2} \right) (A + B\mu^2 M) = 0.$$

Integrating, we get

$$\frac{dv}{dx_1} + A\mu^2 x_1 + B\mu^4 M_1 - A\nu^2 M_3 - B\nu^2 \mu^2 M_4 = 0,$$

where $\mu^2 M_1 = \int_0^{x_1} \mu^2 M_1 dx_1$; $\frac{M_3}{\mu^2} = \int_0^{x_1} \frac{1}{\mu^2} dx_1$; $M_4 = \int_0^{x_1} M dx_1$.

A second integration then gives

$$v + A\mu^2 (x_1 M - M_1) + B\mu^4 M_5 - A\nu^2 M_6 - B\nu^2 \mu^2 M_7 = 0,$$

where $M_5 = \int_0^{x_1} M_1 dx_1$; $M_6 = \int_0^{x_1} M_3 dx_1$; $\mu^2 M_7 = \int_0^{x_1} \mu^2 M_4 dx_1$.

When $x_1 = 0$ all the M 's are zero, and when $x_1 = 1$ we have

$M = E$; $M_1 = H$; $M_3 = F$; $M_4 = J$; $M_5 = K$; $M_6 = L$; $M_7 = N$;
where $E \dots N$ are constants depending on the law of distribution of μ in the layer.

Thus, when $x_1 = 0$ we have

$$u = A; \quad du/dx_1 = B\mu_0^2;$$

and when $x_1 = 1$,

$$u = A + B\mu_1^2 E + d_1^2 [A \{ \mu_1^2 \overline{H} - \overline{E} + \nu^2 L \} + B\mu_1^2 \{ \nu^2 N - \mu_1^2 K \}];$$

$$\frac{du}{dx_1} = B\mu_1^2 + d_1^2 [A (\nu^2 F - \mu_1^2) + B\mu_1^2 (\nu^2 J - \mu_1^2 H)].$$

The boundary conditions give

$$A = 1 + r; \quad B = -id_1 \kappa_0 / \mu_0^2 \cdot (1 - r);$$

$$\mu_1 / \mu_0 \cdot s = A + B\mu_1^2 E + d_1^2 [A \{ \mu_1^2 \overline{H} - \overline{E} + \nu^2 L \} + B\mu_1^2 \{ \nu^2 N - \mu_1^2 K \}]$$

$$-i\kappa_1 \mu_1 / \mu_0 \cdot s = B\mu_1^2 / d_1 + d_1 [A (\nu^2 F - \mu_1^2) + B\mu_1^2 (\nu^2 J - \mu_1^2 H)].$$

Eliminating A and B from these, we get two equations to determine r and s . It will appear later that in most cases we can safely neglect terms containing d_1^2 and higher powers of d_1 . If we do this we get

$$\mu_1 / \mu_0 \cdot s - r [1 + id_1 \kappa_0 E \mu_1^2 / \mu_0^2] = 1 - id_1 \kappa_0 E \mu_1^2 / \mu_0^2;$$

$$\kappa_1 \mu_1 / \mu_0 \cdot s + r [\mu_1^2 / \mu_0^2 \cdot \kappa_0 - id_1 (\nu^2 F - \mu_1^2)] = \kappa_0 \mu_1^2 / \mu_0^2 + id_1 (\nu^2 F - \mu_1^2).$$

Hence

$$s = \mu_0 / \mu_1 \frac{[1 - id_1 \kappa_0 E \mu_1^2 / \mu_0^2] [\kappa_0 \mu_1^2 / \mu_0^2 - id_1 (\nu^2 F - \mu_1^2)]}{\kappa_1 [1 + id_1 \kappa_0 E \mu_1^2 / \mu_0^2] + \mu_1^2 / \mu_0^2 \cdot \kappa_0 - id_1 (\nu^2 F - \mu_1^2)}$$

$$= 2\kappa_0 \mu_1 / \mu_0 \{ (\kappa_1 + \kappa_0 \mu_1^2 / \mu_0^2) + id_1 (E \kappa_0 \kappa_1 \mu_1^2 / \mu_0^2 + \mu_1^2 - \nu^2 F) \}^{-1}, \quad \text{to our order.}$$

$$= Se^{-i\sigma},$$

where
$$S = \frac{2\kappa_0\mu_1/\mu_0}{\kappa_1 + \kappa_0\mu_1^2/\mu_0^2} = \frac{2 \sin \phi_0 \cos \phi_0}{\sin(\phi_0 + \phi_1) \cos(\phi_0 - \phi_1)},$$

and
$$\tan \sigma = \frac{E\kappa_0\kappa_1\mu_1^2/\mu_0^2 + \mu_1^2 - \nu^2 F}{\kappa_1 + \kappa_0\mu_1^2/\mu_0^2} d_1.$$

Thus (to this order) the amplitude is the same as in the *ideal* case of an abrupt transition; but there is a *small* change of phase. Similarly

$$\begin{aligned} r &= \frac{\kappa_0\mu_1^2/\mu_0^2 + id_1(\nu^2 F - \mu_1^2) - \kappa_1(1 - id_1\kappa_0 E\mu_1^2/\mu_0^2)}{\kappa_1(1 + id_1\kappa_0 E\mu_1^2/\mu_0^2) + \mu_1^2\kappa_0/\mu_0^2 - id_1(\nu^2 F - \mu_1^2)} \\ &= Re^{-i\varphi}, \end{aligned}$$

where
$$R = \frac{\kappa_0\mu_1^2/\mu_0^2 - \kappa_1}{\kappa_0\mu_1^2/\mu_0^2 + \kappa_1} = \frac{\tan(\phi_0 - \phi_1)}{\tan(\phi_0 + \phi_1)},$$

and
$$\tan \rho = \frac{(2\kappa_0\mu_1^2/\mu_0^2)[E\kappa_1^2 + F\nu^2 - \mu_1^2]}{\kappa_1^2 - (\kappa_0\mu_1^2/\mu_0^2)^2} d_1,$$

except at the polarising angle, where $\kappa_0\mu_1^2/\mu_0^2 - \kappa_1 = 0$, and we have

$$\rho = \pi/2 \quad \text{and} \quad R = \frac{E\kappa_0\kappa_1\mu_1^2/\mu_0^2 + F\nu^2 - \mu_1^2}{\kappa_1 + \kappa_0\mu_1^2/\mu_0^2} d_1.$$

Here again, in the general case, the amplitude is (to our order of approximation) the same as that given by Fresnel's formula, but there is a small change of phase depending on d_1 . The most marked departure from Fresnel's formula, however, occurs at the polarising angle. In that case R does not vanish as Fresnel gives, but there is a small amount of residual reflected light and the change of phase is $\pi/2$ (a quarter wave-length).

At the polarising angle

$$\begin{aligned} \kappa_1 &= \kappa_0\mu_1^2/\mu_0^2 = \frac{\mu_1^2}{\sqrt{\mu_0^2 + \mu_1^2}}. \\ R &= \frac{d_1}{2\sqrt{\mu_0^2 + \mu_1^2}} [E\mu_1^2 + F\mu_0^2 - (\mu_1^2 + \mu_0^2)] \\ &= \frac{d_1}{2\sqrt{\mu_0^2 + \mu_1^2}} \int_0^1 \frac{(\mu^2 - \mu_0^2)(\mu^2 - \mu_1^2)}{\mu^3} dx_1. \end{aligned}$$

(2) We shall consider in a similar way the case of vibrations *perpendicular* to the plane of incidence (*cf.* p. 51).

In the layer $\zeta' = ue^{ip(t - \nu y/c)}; \quad \xi' = \eta' = 0;$

$$\xi = \frac{\partial \zeta'}{\partial y} = -i \frac{p\nu}{c} ue^{ip(\dots)}; \quad \eta = -\frac{\partial \zeta'}{\partial x} = \frac{du}{dx} e^{ip(\dots)} \quad \zeta = 0;$$

$$f = 0; \quad g = 0; \quad h = -\frac{1}{\mu^2} \nabla^2 \zeta' = \frac{1}{\mu^2} \left[\frac{p^2 \nu^2}{c^2} u - \frac{d^2 u}{dx^2} \right] e^{ip(\dots)}.$$

$$\xi = c^2 \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right) = c^2 \frac{\partial}{\partial y} \left(\frac{1}{\mu^2} \nabla^2 \zeta' \right) \therefore \frac{\partial}{\partial y} \left[\zeta' - \frac{c^2}{\mu^2} \nabla^2 \zeta' \right] = 0.$$

$$\eta = c^2 \left(\frac{\partial h}{\partial x} - \frac{\partial f}{\partial z} \right) = -c^2 \frac{\partial}{\partial x} \left(\frac{1}{\mu} \nabla^2 \zeta' \right) \therefore \frac{\partial}{\partial x} \left[\zeta' - \frac{c^2}{\mu^2} \nabla^2 \zeta' \right] = 0.$$

These equations are satisfied if $\zeta' - \frac{c^2}{\mu^2} \nabla^2 \zeta' = 0$. Hence

$$\frac{d^2 u}{dx^2} + \frac{p^2}{c^2} (\mu^2 - \nu^2) u = 0, \text{ or } \frac{d^2 u}{dx_1^2} + d_1^2 (\mu^2 - \nu^2) u = 0 \dots\dots\dots (iii).$$

Solving (iii) by approximations, we get first $d^2 u/dx_1^2 \approx 0$, so that $u = A + Bx_1$ and, as a second approximation,

$$u = A + Bx_1 + d_1^2 v, \text{ where } d^2 v/dx_1^2 + (\mu^2 - \nu^2)(A + Bx_1) = 0 \dots (iv).$$

Now
$$\int x_1 \mu^2 dx_1 = x_1 \mu^2 M - \int \mu^2 M dx_1 = \mu^2 (x_1 M - M_1).$$

Hence on integrating (iv), we get

$$\frac{dv}{dx_1} = \nu^2 (Ax_1 + \frac{1}{2} Bx_1^2) - \mu^2 (AM + Bx_1 M - BM_1)$$

and
$$v = \nu^2 (Ax_1^2 + Bx_1^3) - \mu^2 (AM_1 + Bx_1 M_1 - 2BM_2),$$

where
$$\mu^2 M_2 = \int_0^{x_1} \mu^2 M_1 dx_1.$$

When $x_1 = 0$, $M_2 = 0$, and when $x_1 = 1$, $M_2 = G$. Thus we have

when $x_1 = 0$, $u = A$; $du/dx_1 = B$;

and when $x_1 = 1$,

$$u = A + B + d_1^2 [\nu^2 (\frac{1}{2} A + \frac{1}{6} B) - \mu_1^2 (A + B \cdot H - 2BG)];$$

$$du/dx = B + d_1^2 [\nu^2 (A + \frac{1}{2} B) - \mu_1^2 (A + B \cdot E - BH)].$$

The boundary conditions give

$$A = 1 + r'; \quad B = -id_1 \kappa_0 (1 - r');$$

$$s' = A + B + d_1^2 [\nu^2 (\frac{1}{2} A + \frac{1}{6} B) - \mu_1^2 (A + B \cdot H - 2BG)]$$

$$-id_1 \kappa_1 s' = B + d_1^2 [\nu^2 (A + \frac{1}{2} B) - \mu_1^2 (A + B \cdot E - BH)].$$

Eliminating A and B from these equations, we get two equations to determine r' and s' . If, as before, we retain only the first power of d_1 , we get

$$s' - r' [1 + id_1 \kappa_0] = 1 - id_1 \kappa_0;$$

$$\kappa_1 s' + r' [\kappa_0 + id_1 (E\mu_1^2 - \nu^2)] = \kappa_0 - id_1 (E\mu_1^2 - \nu^2).$$

Thus

$$\begin{aligned} s' &= \frac{[1 - id_1 \kappa_0][\kappa_0 + id_1(E\mu_1^2 - \nu^2)] + [1 + id_1 \kappa_0][\kappa_0 - id_1(E\mu_1^2 - \nu^2)]}{[\kappa_0 + id_1(E\mu_1^2 - \nu^2)] + \kappa_1[1 + id_1 \kappa_0]} \\ &= 2\kappa_0 / \{(\kappa_0 + \kappa_1) + id_1(\kappa_0 \kappa_1 + E\mu_1^2 - \nu^2)\} \\ &= S'e^{-i\sigma'}, \end{aligned}$$

where

$$S' = \frac{2\kappa_0}{\kappa_0 + \kappa_1} = \frac{2 \sin \phi_0 \cos \phi_0}{\sin(\phi_0 + \phi_1)},$$

and

$$\tan \sigma' = \frac{\kappa_0 \kappa_1 + E\mu_1^2 - \nu^2}{\kappa_0 + \kappa_1}.$$

$$\text{Similarly } r' = \frac{\kappa_0 - id_1(E\mu_1^2 - \nu^2) - \kappa_1(1 - id_1 \kappa_1)}{\kappa_0 + \kappa_1 + id_1(\kappa_0 \kappa_1 + E\mu_1^2 - \nu^2)} = R'e^{-i\sigma'},$$

where

$$R' = \frac{\kappa_1 - \kappa_0}{\kappa_1 + \kappa_0} = -\frac{\sin(\phi_1 - \phi_0)}{\sin(\phi_1 + \phi_0)}$$

and

$$\begin{aligned} \tan \rho' &= \left[\frac{\kappa_0 \kappa_1 + E\mu_1^2 - \nu^2}{\kappa_1 + \kappa_0} + \frac{\kappa_0 \kappa_1 - E\mu_1^2 + \nu^2}{\kappa_1 - \kappa_0} \right] d_1 \\ &= \frac{2\kappa_0(\kappa_1^2 + \nu^2 - E\mu_1^2)}{\kappa_1^2 - \kappa_0^2} d_1 = \frac{2\kappa_0 \mu_1^2(1 - E)}{\mu_1^2 - \mu_0^2} d_1. \end{aligned}$$

As before, the amplitude is the same as that given by Fresnel, but there is a small change of phase.

If Δ_1 be the difference of phase between the parallel and perpendicular vibrations for reflection, and Δ_2 that for refraction, we have

$$\tan \Delta_1 = \tan(\rho - \rho') = \tan \rho - \tan \rho', \text{ since } \rho \text{ and } \rho' \text{ are small.}$$

$$= 2\kappa_0 \mu_1^2 d_1 \left[\frac{E\kappa_1^2 + F\nu^2 - \mu_1^2}{\mu_0^2 \{-(\kappa_0 \mu_1^2 / \mu_0^2)^2 + \kappa_1^2\}} - \frac{1 - E}{\mu_1^2 - \mu_0^2} \right],$$

$$\tan \Delta_2 = \tan(\sigma - \sigma') = \tan \sigma - \tan \sigma'.$$

$$= d_1 \left[\frac{E\kappa_0 \kappa_1 \mu_1^2 / \mu_0^2 + \mu_1^2 - \nu^2 F}{\kappa_1 + \kappa_0 \mu_1^2 / \mu_0^2} - \frac{\kappa_0 \kappa_1 + E\mu_1^2 - \nu^2}{\kappa_0 + \kappa_1} \right],$$

except near the polarising angle, where $\rho = \pi/2$ and $\Delta_1 = \pi/2 - \rho'$.

The above results show that ϵ_1 and ϵ_2 are the same as given by Fresnel's formulæ, except in the neighbourhood of the polarising angle when ϵ_1 is not zero, but is very small. At the polarising angle we have

$$\epsilon_1 = \frac{R}{R'} = -\frac{d_1}{2} \frac{\sqrt{\mu_1^2 + \mu_0^2}}{\mu_1^2 - \mu_0^2} \int_0^1 \left[\mu^2 + \frac{\mu_1^2 \mu_0^2}{\mu^2} - (\mu_0^2 + \mu_1^2) \right] dx_1.$$

We see from this that ϵ_1 is a maximum along with $\mu^2 + \frac{\mu_1^2 \mu_0^2}{\mu^2}$, i.e., when $\mu^2 = \mu_0 \mu_1$. If μ^2 had this value throughout, we should have

$$\epsilon_1 = \frac{d_1}{2} \frac{\mu_1 - \mu_0}{\mu_1 + \mu_0} \sqrt{\mu_1^2 + \mu_0^2} = \frac{\pi d}{\lambda_0 \mu_0} \frac{\mu_1 - \mu_0}{\mu_1 + \mu_0} \sqrt{\mu_1^2 + \mu_0^2}.$$

This enables us to obtain an upper limit for the value of d/λ_0 necessary to produce the observed ellipticity at the polarising angle. Taking Kurz's experiments on reflection from glass into air, we have $\mu_0 = 1$, $\mu_1 = 1.5963$, $\epsilon_1 = \tan 1^\circ 58' = 0.0344$. This gives $d/\lambda_0 = 0.0025$ and $d_1 = 0.0159$. With Jamin's experiments on reflection from diamond into air $\mu_0 = 1$, $\mu_1 = 2.434$, $\epsilon_1 = \tan 1^\circ 21' = 0.0236$, which gives $d/\lambda_0 = 0.0074$ and $d_1 = 0.0464$. In the case of glass d_1^2 is about one-hundredth of ϵ_1 , while with diamond d_1^2 is about one-tenth of ϵ_1 . In the latter case it would not be satisfactory for accurate work to neglect d_1^2 in the determination of the ellipticity, so that it may be advisable to conduct the calculations to a higher order of approximation, retaining d_1^2 .

We have

$$\begin{aligned} \mu_1/\mu_0 \cdot s - r [1 + id_1\kappa_0 E \mu_1^2/\mu_0^2 + d_1^2 (\mu_1^2 \overline{H} - \overline{E} + \nu^2 L)] \\ = 1 - id_1\kappa_0 E \mu_1^2/\mu_0^2 + d_1^2 (\mu_1^2 \overline{H} - \overline{E} + \nu^2 L); \\ \kappa_1 \mu_1/\mu_0 \cdot s + r [\mu_1^2 \kappa_0/\mu_0^2 - id_1 (\nu^2 F - \mu_1^2) + \mu_1^2/\mu_0^2 \cdot \kappa_0 d_1^2 (\nu^2 J - \mu_1^2 H)] \\ = \kappa_0 \mu_1^2/\mu_0^2 + id_1 (\nu^2 F - \mu_1^2) + \mu_1^2/\mu_0^2 \cdot \kappa_0 d_1^2 (\nu^2 J - \mu_1^2 H). \\ [1 - id_1\kappa_0 E \mu_1^2/\mu_0^2 + d_1^2 (\mu_1^2 \overline{H} - \overline{E} + \nu^2 L)] \\ [\kappa_0 - id_1 \mu_0^2/\mu_1^2 \cdot (\nu^2 F - \mu_1^2) + \kappa_0 d_1^2 (\nu^2 J - \mu_1^2 H)] \\ + [1 + id_1\kappa_0 E \mu_1^2/\mu_0^2 + d_1^2 (\mu_1^2 \overline{H} - \overline{E} + \nu^2 L)] \\ \therefore s = \frac{\mu_1}{\mu_0} \frac{[\kappa_0 + id_1 \mu_0^2/\mu_1^2 \cdot (\nu^2 F - \mu_1^2) + \kappa_0 d_1^2 (\nu^2 J - \mu_1^2 H)]}{\kappa_0 [1 + id_1\kappa_0 E \mu_1^2/\mu_0^2 + d_1^2 (\mu_1^2 \overline{H} - \overline{E} + \nu^2 L)] \\ + \mu_1^2/\mu_0^2 \cdot [\kappa_0 - id_1 \mu_0^2/\mu_1^2 \cdot (\nu^2 F - \mu_1^2) + \kappa_0 d_1^2 (\nu^2 J - \mu_1^2 H)]} \\ = \frac{2\kappa_0 \mu_1/\mu_0 \cdot [1 + d_1^2 (\nu^2 L + J + \overline{E}H) - 2E \mu_1^2]}{(\kappa_1 + \kappa_0 \mu_1^2/\mu_0^2) + id_1 (-\nu^2 F + \mu_1^2 + E \kappa_0 \mu_1^2/\mu_0^2) \\ + d_1^2 [\kappa_1 (\mu_1^2 \overline{H} - \overline{E} + \nu^2 L) + \kappa_0 \mu_1^2/\mu_0^2 \cdot (\nu^2 J - \mu_1^2 H)]} \\ = S e^{-i\sigma}, \end{aligned}$$

where

$$S = \frac{2\kappa_0 \mu_1/\mu_0}{\kappa_1 + \kappa_0 \mu_1^2/\mu_0^2} \left[1 + d_1^2 \left\{ \nu^2 (L + J + \overline{E}H) - 2E \mu_1^2 \right. \right. \\ \left. \left. - \frac{(\kappa_0 \kappa_1 \mu_1^2/\mu_0^2 - \nu^2 F + \mu_1^2) + 2(\kappa_1 + \kappa_0 \mu_1^2/\mu_0^2) \{ \kappa_1 (\mu_1^2 \overline{H} - \overline{E} + \nu^2 L) \right. \right. \\ \left. \left. + \kappa_0 \mu_1^2/\mu_0^2 (\nu^2 J - \mu_1^2 H) \}}{2(\kappa_1 + \kappa_0 \mu_1^2/\mu_0^2)} \right\} \right],$$

$$\text{and} \quad \tan \sigma = \frac{E \kappa_0 \mu_1^2/\mu_0^2 + \mu_1^2 - \nu^2 F}{\kappa_1 + \kappa_0 \mu_1^2/\mu_0^2} d_1.$$

Similarly

$$\begin{aligned} & \kappa_0 \mu_1^2 / \mu_0^2 + i d_1 (\nu^2 F - \mu_1^2) + \mu_1^2 / \mu_0^2 \cdot \kappa_0 d_1^2 (\nu^2 J - \mu_1^2 H) \\ r = & \frac{-\kappa_1 [1 - i d_1 \kappa_0 E \mu_1^2 / \mu_0^2 + d_1^2 (\mu_1^2 \bar{H} - \bar{E} + \nu^2 L)]}{(\kappa_1 + \mu_1^2 / \mu_0^2 \kappa_0) + i d_1 (-\nu^2 F + \mu_1^2 + E \kappa_0 \kappa_1 \mu_1^2 / \mu_0^2) \\ & + d_1^2 [\kappa_1 (\mu_1^2 \bar{H} - \bar{E} + \nu^2 L) + \kappa_0 \mu_1^2 / \mu_0^2 \cdot (\nu^2 J - \mu_1^2 H)]} \\ = & R e^{-i\rho}, \end{aligned}$$

where

$$\begin{aligned} R = & \frac{\kappa_0 \mu_1^2 / \mu_0^2 - \kappa_1}{\kappa_0 \mu_1^2 / \mu_0^2 + \kappa_1} \left[1 + \frac{2 \kappa_0 \kappa_1 \mu_1^2 / \mu_0^2 \cdot d_1^2}{(\kappa_0^2 \mu_1^4 / \mu_0^4 - \kappa_1^2)^2} \right. \\ & \left. \left\{ (\kappa_0 \kappa_1 E \mu_1^2 / \mu_0^2)^2 + (\mu_1^2 - \nu^2 F)^2 - E (\mu_1^2 - \nu^2 F) (\kappa_0^2 \mu_1^4 / \mu_0^4 + \kappa_1^2) \right\} \right. \\ & \left. + (\kappa_0^2 \mu_1^4 / \mu_0^4 - \kappa_1^2) (\nu^2 J - L + \mu_1^2 \cdot \bar{E} - 2H) \right] \end{aligned}$$

and

$$\tan \rho = \frac{2 \kappa_0 \mu_1^2 / \mu_0^2 \cdot (E \kappa_1^2 + F \nu^2 - \mu_1^2)}{\kappa_1^2 - \kappa_0^2 \mu_1^4 / \mu_0^4} d_1,$$

except at the polarising angle, where

$$\kappa_1 = \mu_1^2 / \mu_0 \kappa_0 \quad \text{and} \quad R = \frac{\kappa_0 \kappa_1 E \mu_1^2 / \mu_0^2 - \mu_1^2 + \nu^2 F}{\kappa + \kappa_0 \mu_1^2 / \mu_0^2} d_1.$$

$$\rho = \frac{\pi}{2} - \theta,$$

$$\begin{aligned} \tan \theta = & d_1 \frac{[\kappa_0 \mu_1^2 / \mu_0^2 \cdot (\nu^2 J - \mu_1^2 H) - \kappa_1 (\mu_1^2 \bar{H} - \bar{E} + \nu^2 L)] (\kappa_1 + \kappa_0 \mu_1^2 / \mu_0^2)}{(\kappa_1 + \kappa_0 \mu_1^2 / \mu_0^2) (\kappa_0 \kappa_1 E \mu_1^2 / \mu_0^2 - \mu_1^2 + \nu^2 F)} \\ & + [(\kappa_0 \kappa_1 E \mu_1^2 / \mu_0^2)^2 - (\mu_1^2 - \nu^2 F)^2] \\ = & \frac{d_1}{\sqrt{\mu_0^2 + \mu_1^2}} \frac{2 \mu_1^2 [J - 2H - L] + \mu_1^2 (E - 2H) + E^2 \mu_1^4}{E \mu_1^2 - (\mu_0^2 + \mu_1^2 - \mu_0^2 F)} \end{aligned}$$

For vibrations perpendicular to the plane of incidence, we have, in like manner,

$$\begin{aligned} & [1 - i d_1 \kappa_0 - d_1^2 (H \mu_1^2 - \nu^2 / 2)] [\kappa_0 + i d_1 (E \mu_1^2 - \nu^2) + \kappa_0 d_1^2 (\nu^2 / 2 + \bar{H} - \bar{E} \mu_1^2)] \\ & + [1 + i d_1 \kappa_0 - d_1^2 (H \mu_1^2 - \nu^2 / 2)] \\ s' = & \frac{\times [\kappa_0 - i d_1 (E \mu_1^2 + \nu^2) + \kappa_0 d_1^2 (\nu^2 / 2 + \bar{H} - \bar{E} \mu_1^2)]}{\kappa_0 + i d_1 (E \mu_1^2 - \nu^2) + \kappa_0 d_1^2 (\nu^2 / 2 + \bar{H} - \bar{E} \mu_1^2) + \kappa_1 [1 + i d_1 \kappa_0 - d_1^2 (H \mu_1^2 + \nu^2 / 2)]} \\ = & \frac{2 \kappa_0}{(\kappa_0 + \kappa_1) + i d_1 (\kappa_0 \kappa_1 + E \mu_1^2 - \nu^2) + d_1^2 [\kappa_0 + \kappa_1 \nu^2 / 2 - \mu_1^2 (E \kappa_0 + H \kappa_1 - H \kappa_0)]} \\ = & S' e^{-i\omega'}, \end{aligned}$$

where

$$\begin{aligned} S' = & \frac{2 \kappa_0}{\kappa_0 + \kappa_1} \left[1 - \frac{d_1^2}{2 (\kappa_0 + \kappa_1)^2} \right. \\ & \left. \left\{ (\kappa_0 \kappa_1 + E \mu_1^2 - \nu^2)^2 + (\kappa_0 + \kappa_1) (\kappa_0 + \kappa_1 \cdot \nu^2 - 2 \mu_1^2 \cdot \overline{E \kappa_0 + H \kappa_1 - H \kappa_0}) \right\} \right] \end{aligned}$$

$$\tan \sigma' = \frac{\kappa_0 \kappa_1 + E \mu_1^2 - \nu^2}{\kappa_0 + \kappa_1} d_1,$$

$$\begin{aligned} \text{and } r' &= \frac{[\kappa_0 - i d_1 (E \mu_1^2 - \nu^2) + \kappa_0 d_1^2 (\nu^2/2 + \overline{H - E \mu_1^2})] \\ &\quad - \kappa_1 [1 - i d_1 \kappa_0 - d_1^2 (H \mu_1^2 - \nu^2/2)]}{(\kappa_0 + \kappa_1) + i d_1 (\kappa_0 \kappa_1 + E \mu_1^2 - \nu^2) \\ &\quad + d_1^2 [(\kappa_0 + \kappa_1) \nu^2/2 - \mu_1^2 (E \kappa_0 + H \cdot \overline{\kappa_1 - \kappa_0})]} \\ &= - \frac{(\kappa_1 - \kappa_0) - i d_1 (\kappa_0 \kappa_1 - E \mu_1^2 + \nu^2) \\ &\quad + d_1^2 [(\kappa_1 - \kappa_0) \nu^2/2 - \mu_1^2 (E \kappa_0 - H \cdot \overline{\kappa_1 - \kappa_0})]}{(\kappa_1 + \kappa_0) + i d_1 (\kappa_0 \kappa_1 + E \mu_1^2 - \nu^2) \\ &\quad + d_1^2 [(\kappa_0 + \kappa_1) \nu^2/2 - \mu_1^2 (E \kappa_0 + H \overline{\kappa_1 - \kappa_0})]} \\ &= R' e^{-i\phi'}, \end{aligned}$$

where

$$R' = \frac{\kappa_1 - \kappa_0}{\kappa_1 + \kappa_0} \left[1 + \frac{2 \kappa_0 \kappa_1 d_1^2}{(\kappa_1^2 - \kappa_0^2)} \left\{ \kappa_0^2 \kappa_1^2 + (E \mu_1^2 - \nu^2)^2 + \mu_1^2 (E - 2H) (\kappa_1^2 - \kappa_0^2) - (E \mu_1^2 - \nu^2) (\kappa_1^2 + \kappa_0^2) \right\} \right],$$

$$\begin{aligned} \text{and } \tan \rho' &= d_1 \left[\frac{\kappa_0 \kappa_1 + E \mu_1^2 - \nu^2}{\kappa_1 + \kappa_0} + \frac{\kappa_0 \kappa_1 - E \mu_1^2 + \nu^2}{\kappa_1 - \kappa_0} \right] \\ &= 2 \kappa_0 d_1 \frac{\kappa_1^2 + \nu^2 - E \mu_1^2}{\kappa_1^2 - \kappa_0^2} = 2 \kappa_0 d_1 \frac{\mu_1^2 (1 - E)}{\mu_1^2 - \mu_0^2}. \end{aligned}$$

It will be observed that the retardations of phase (ρ , ρ' , σ , σ') are the same as to the first approximation, except that at the polarising angle ρ is $\frac{\pi}{2} - \theta$ instead of $\frac{\pi}{2}$.

On examining the various formulæ thus obtained, it becomes apparent that it will not be possible to calculate the constants d_1 , E , F , etc., so as to fit in with experimental results with much accuracy. Of the quantities depending on these constants it is only ϵ_1 (the ellipticity) and ρ the retardation of phase that are large enough to be measured with accuracy, and even with these the departure from Fresnel's formulæ is appreciable only within a few degrees of the polarising angle. Hence, instead of applying these results directly, we shall derive from them much simpler formulæ for ϵ_1 and ρ —formulæ which involve only a single arbitrary constant, and which colligate the experimental results well within the limits of errors of observation.*

In the expression for $\tan \rho$ the factor $2 (E \kappa_1^2 + F \nu^2 - \mu_1^2)$ is equal to $-\mu_1^2 [(F - E) \cos 2\phi_1 + (2 - E - F)]$. Now $F - E$ is not very large, for F cannot be greater than μ_1^2 , nor E less than $1/\mu_1^2$. Thus for a variation of

* See the graphs on pp. 64-5.

a few degrees in ϕ_0 , the expression $(F-E) \cos 2\phi_1$ is practically constant. Putting $4d_1 [(F-E) \cos 2\phi_1 + 2 - E - F] = e$, we have these simple formulæ for ρ and ϵ_1 —

$$\tan \rho = \frac{e \sin^2 \phi_0 \cos \phi_0}{\sin 2(\phi_0 + \phi_1) \sin 2(\phi_0 - \phi_1)}. \quad (A)$$

$$\epsilon_1 = \tan \omega = \frac{R}{R'} = -\frac{\sin(\phi_0 + \phi_1)}{\sin(\phi_0 - \phi_1)} \frac{\sqrt{(\cos \phi_0 - \mu_0/\mu_1 \cdot \cos \phi_1)^2 + (e/8)^2}}{\cos \phi_0 + \mu_0/\mu_1 \cdot \cos \phi_1}. \quad (B)$$

If we put $r = x - iy = Re^{-i\omega}$, then we have very approximately,

$$x = \frac{\tan(\phi_0 - \phi_1)}{\tan(\phi_0 + \phi_1)} \quad (\text{the } r \text{ of Fresnel}).$$

$$y = \frac{d_1 (E\kappa_0\kappa_1\mu_1^2/\mu_0^2 + F\nu^2 - \mu_1^2)}{\kappa_1 + \kappa_0\mu_1^2/\mu_0^2} = \frac{e/8}{\cos \phi_0 + \mu_0/\mu_1 \cdot \cos \phi_1}. \quad (C)$$

The denominator in y will vary very little throughout a considerable range on each side of the polarising angle, so that throughout this range y will be very nearly constant. Hence, if we draw a graph to represent the amplitude and phase of the reflected light (the vibrations being parallel to the plane of incidence), we get very approximately a straight line parallel to the axis of x , and all the points of departure from Fresnel's formulæ are indicated—as regards both amplitude and phase—by the slight shifting of a straight line from the axis of x to a parallel position.*

We shall apply these formulæ to the case of reflection and refraction where the media are diamond and air, and compare the theoretical results with Jamin's experiments on reflection with these media.

We have $\mu_0 = 1$; $\mu_1 = 2.434$; the polarising angle is $67^\circ 40'$.

Taking $e = 0.105$, we get the following table for the ellipticity in the neighbourhood of the polarising angle, the theoretical value being calculated from the formula B, above:—

ϕ_0	Theory. $\omega = \tan^{-1}\epsilon_1$	Experiment. ω	Difference.	Theory. ϵ_1^2	Experiment. ϵ_1^2	Difference.
$66^\circ 0'$	$-3^\circ 8'$	$-3^\circ 9'$	$+ 6'$	0.00282	0.00303	-0.00021
$66^\circ 30'$	$-2^\circ 21'$	$-2^\circ 23'$	$+ 2'$	0.00168	0.00173	-0.00005
$67^\circ 0'$	$-1^\circ 45'$	$-1^\circ 45'$	0	0.00093	0.00092	0
$67^\circ 30'$	$-1^\circ 25'$	$-1^\circ 22'$	$- 3'$	0.00061	0.00057	$+0.00004$
$68^\circ 0'$	$+1^\circ 30'$	$+1^\circ 30'$	0	0.00068	0.00068	0
$68^\circ 30'$	$+2^\circ 2'$	$+2^\circ 3'$	$- 1'$	0.00126	0.00128	-0.00002
$69^\circ 0'$	$+2^\circ 34'$	$+2^\circ 57'$	$-23'$	0.00200	0.00265	-0.00065

* See graph, p. 65.

Outside of this range the ellipticity is given sufficiently accurately by Fresnel's formula, as the following table will show :—

ϕ_0	Theory (Fresnel). ω .	Experiment. ω .	Difference.	Theory (Fresnel). ϵ_1^2 .	Experiment. ϵ_1^2 .	Difference.
60	—11 36	—11 35	—1	0·04218	0·04202	+0·00011
61	—10 12	—10 1	—11	0·03238	0·03120	+0·00118
62	—8 48	—8 18	—30	0·02397	0·02128	+0·00269
63	—7 21	—7 36	+15	0·01664	0·01780	—0·00116
64	—5 50	—5 46	—4	0·01043	0·01020	+0·00023
65	—4 17	—4 20	+3	0·00561	0·00574	—0·00013
70	+4 0	+4 11	—11	0·00489	0·00535	—0·00046
71	+5 47	+5 53	—6	0·01026	0·01062	—0·00036
72	+7 35	+7 44	—9	0·01772	0·01844	—0·00072
73	+9 25	+9 46	—21	0·02751	0·02963	—0·00212
74	+11 18	+12 13	—55	0·03992	0·04688	—0·00696
75	+13 13	+13 30	—17	0·05516	0·05762	—0·00246

The following table gives the retardation of phase ρ calculated from the formula (A) of p. 61. The column headed " ρ " gives the retardation expressed as an angle, that headed " ρ/π " gives the retardation in fractions of the half wave-length :—

ϕ_0	ρ	ρ/π	ϕ_0	ρ	ρ/π
60 0	7 17	0·0406	68 0	112 26	0·6243
61 0	8 14	0·0457	68 30	135 50	0·7544
62 0	9 28	0·0527	69 0	149 0	0·8277
63 0	11 14	0·0624	70 0	161 26	0·8966
64 0	13 55	0·0772	71 0	167 8	0·9283
65 0	18 30	0·1028	72 0	170 19	0·9458
66 0	27 46	0·1544	73 0	172 21	0·9570
66 30	36 27	0·2031	74 0	173 48	0·9654
67 0	51 49	0·2877	75 0	174 50	0·9709
67 30	78 30	0·4361			

If $\text{Re}^{-\phi} = x - iy$, we have the following values of x and y calculated from the formula (C) of p. 61 :—

ϕ_0	x	y	ϕ_0	x	y
60	0·1814	0·01681	68	—0·0071	0·01727
61	0·1162	0·01689	69	—0·0287	0·01728
62	0·1016	0·01695	70	—0·0514	0·01726
63	0·0858	0·01704	71	—0·0754	0·01723
64	0·0690	0·01710	72	—0·1007	0·01718
65	0·0513	0·01716	73	—0·1247	0·01674
66	0·0328	0·01728	74	—0·1525	0·01695
67	0·0136	0·01726			

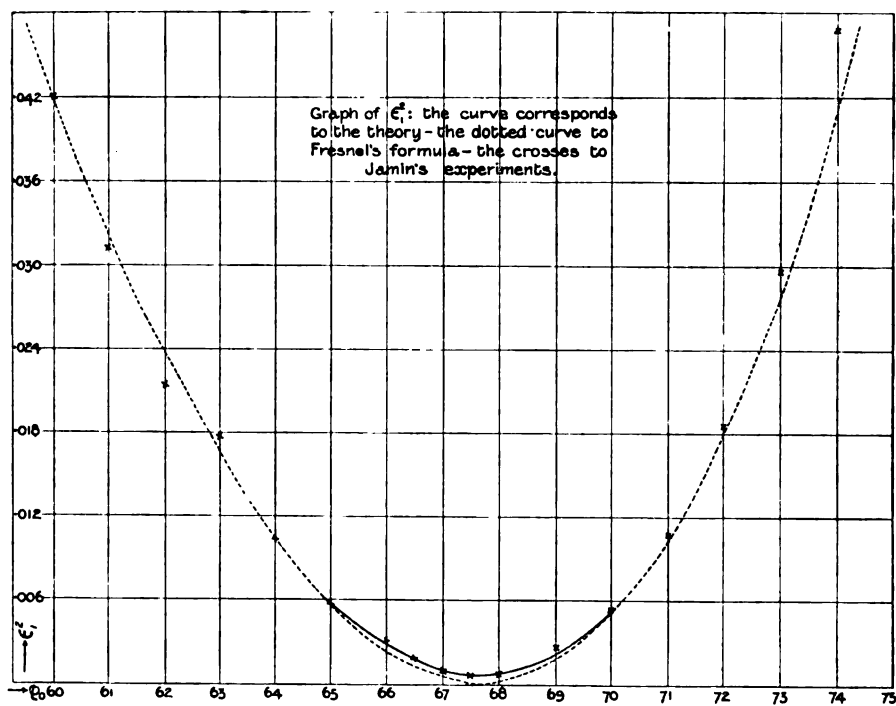
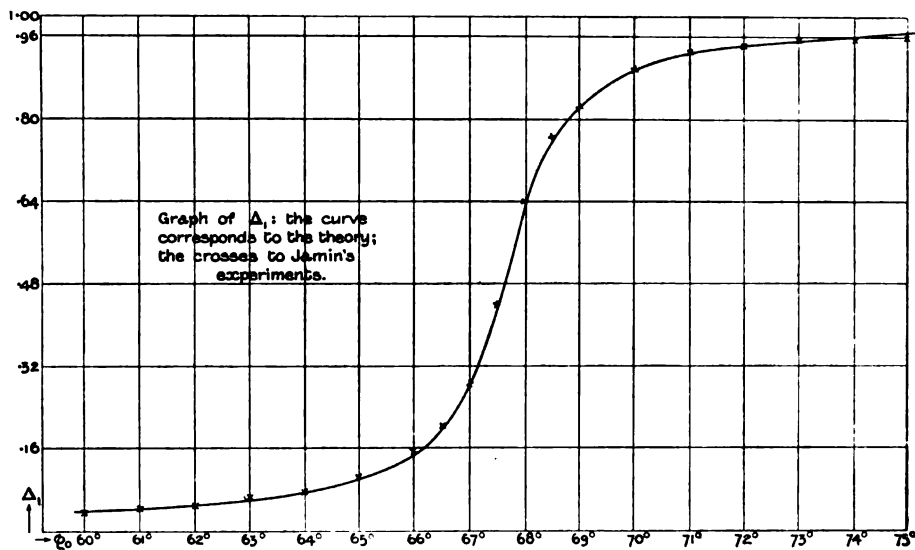
It has been remarked before that the constants d_1 , E , F cannot be determined very accurately. We have seen that d_1 is less than 0.046. Further, we have $e/8d_1 = 1 - 0.8616E - 0.144F$, and since E and F must be positive, we must have $e/8d_1 < 1$, so that $d_1 > e/8$. If $e = 0.105$, this gives $d_1 > 0.013$, so that d_1 must lie between 0.013 and 0.046.

We shall take $E = 0.5$, $F = 1.8$, $d_1 = 0.0412$, and calculate ρ' , σ , and σ' from the formulæ of pp. 55 and 57.

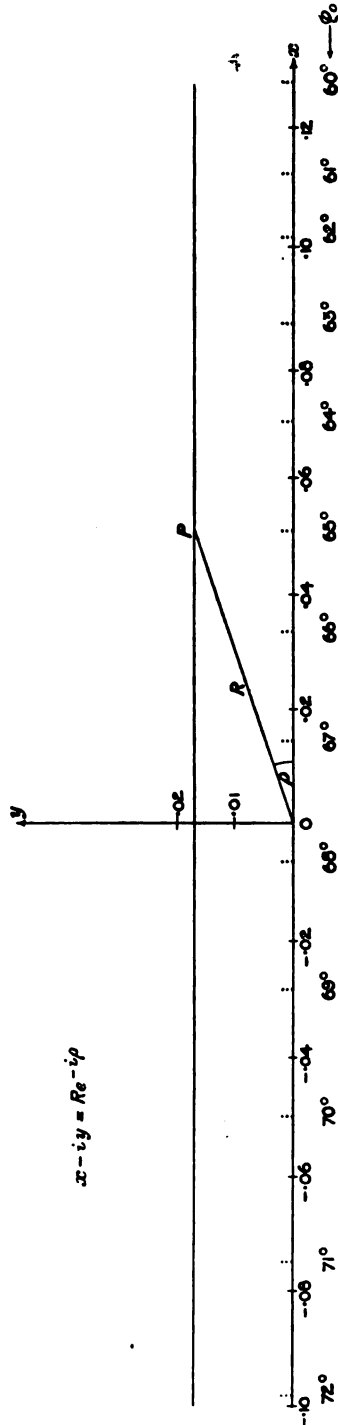
ϕ_0	$-\sigma$	σ'	$-\sigma/\pi$	σ'/π	$-\Delta_2 = (\sigma' - \sigma)/\pi$
60	1 12	6 0	0.0067	0.0838	0.0400
61	1 13	6 8	0.0068	0.0836	0.0404
62	1 15	6 5	0.0069	0.0838	0.0407
63	1 16	6 8	0.0070	0.0841	0.0411
64	1 18	6 10	0.0072	0.0842	0.0418
65	1 19	6 18	0.0073	0.0845	0.0418
66	1 21	6 16	0.0075	0.0848	0.0423
67	1 23	6 18	0.0077	0.0850	0.0427
68	1 25	6 21	0.0079	0.0852	0.0431
69	1 26	6 24	0.0080	0.0855	0.0435
70	1 28	6 28	0.0083	0.0859	0.0442
71	1 30	6 29	0.0083	0.0860	0.0443
72	1 32	6 32	0.0085	0.0863	0.0448
73	1 35	6 35	0.0088	0.0868	0.0454
74	1 38	6 38	0.0091	0.0868	0.0459
75	1 40	6 41	0.0092	0.0871	0.0463

The following table gives the value of ρ' and the difference of phase Δ_1 (expressed as a fraction of the half wave-length) between the parallel and perpendicular vibrations, compared with Jamin's observations on reflection:—

ϕ_0	ρ'	ρ'/π	$\Delta_1 = (\rho - \rho')/\pi$ Theory.	Δ_1 Experiment.	Difference.
60 0	1 25	0.0078	0.0828	0.082	+0.0008
61 0	1 23	0.0076	0.0881	0.042	-0.0089
62 0	1 20	0.0074	0.0453	0.047	-0.0047
63 0	1 17	0.0071	0.0558	0.063	-0.0077
64 0	1 14	0.0069	0.0708	0.073	-0.0027
65 0	1 12	0.0067	0.0961	0.105	-0.0069
66 0	1 9	0.0064	0.1480	0.155	-0.0070
66 30	1 8	0.0063	0.1968	0.202	-0.0052
67 0	1 7	0.0061	0.2816	0.288	-0.0064
67 30	1 5	0.0060	0.4801	0.437	-0.0069
68 0	1 4	0.0059	0.6184	0.640	-0.0216
68 30	1 3	0.0058	0.7486	0.769	-0.0204
69 0	1 1	0.0056	0.8221	0.826	-0.0089
70 0	0 59	0.0055	0.8911	0.897	-0.0069
71 0	0 56	0.0052	0.9231	0.928	-0.0049
72 0	0 53	0.0050	0.9408	0.940	+0.0008
73 0	0 50	0.0046	0.9524	0.948	+0.0044
74 0	0 47	0.0045	0.9609	0.955	+0.0059
75 0	0 44	0.0041	0.9668	0.962	+0.0048



Graph representing the amplitude and phase of the reflected light, the vibrations being parallel to the plane of incidence.
 OP represents the ratio of the amplitude of the reflected wave to that of the incident wave, and the angle POz represents the retardation of phase.



*On the Relation between Variations of Atmospheric Pressure in
North-East Africa and the Nile Flood.*

By Captain H. G. LYONS, Director-General Survey Department of Egypt.

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[PLATE 1.]

Introductory.—The relation of pressure variations to precipitation and the similarity of such variations over wide areas have been studied by several investigators.

In presenting the evidence of variation of climate,* Brückner has shown that in every period of greater rainfall there is a reduction of the differences of atmospheric pressure between stations, while in every dry period there is an increase, and these variations occur both in the differences of pressure between one station and another, and between different seasons.

Sir N. Lockyer and Dr. W. J. Lockyer have discussed periodic variations of pressure in a series of communications to the Royal Society,† wherein they point out that these variations of pressure over the Indian Ocean and neighbouring regions are inverse in character to those which occur in the American area, while certain other regions are intermediate in type.

Dr. F. H. Bigelow has recently dealt with‡ the synchronism of the variations of the solar prominences with terrestrial atmospheric pressures, and concludes that "the phenomenon of inversion prevails in the earth's atmosphere, localizing the effect of solar action in two typical curves which are the inverse of one another." The distribution of his direct, indirect, and indifferent types agrees closely with that published by Sir N. Lockyer§ in his paper "On the Behaviour of the Short-Period Atmospheric Pressure Variation over the Earth's Surface."

In 1895, Sir J. Eliot published|| a preliminary discussion of oscillatory changes of pressure in India, and showed that¶ well marked oscillations, having a period of more than a year, occur over the Indian area, and are

* 'Klimaschwankungen,' Vienna, 1890, p. 218.

† "On some Phenomena which suggest a Short Period of Solar and Meteorological Changes," 'Roy. Soc. Proc.,' vol. 70, p. 501.

‡ 'Monthly Weather Review,' November, 1903, p. 509.

§ 'Roy. Soc. Proc.,' vol. 73, p. 467, 1904.

|| 'Indian Meteorological Memoirs,' vol. 6, Part II.

¶ *Loc. cit.*, p. 117.

directly related to the character and distribution of precipitation over the Indian monsoon area, and to the great atmospheric movements over India. Recently, Professor J. Hann has studied* the relation between the variations of pressure in Iceland and the weather conditions in north-western Europe.

Object of the Present Paper.—The object of the present paper is to show that similar pressure anomalies stand in close relation to the excess or deficit of the monsoon rainfall of Abyssinia, and consequently to the Nile flood, which is the direct result of the Abyssinian rainfall. Until recently, the problem has been complicated by the assumption, based on the discharge measurements of Linant de Bellefonds and others, that the volume which the White Nile contributed to the flood was not very greatly inferior to that furnished by the Blue Nile, and consequently the rainfall of the basin of the White Nile and its tributaries must be considered. Now, however, it is known that the volume of the White Nile is held back by the Blue Nile when in flood, and the supply it furnishes is practically negligible until the discharge of the Blue Nile falls below 3000 or 4000 cubic metres per second, that is about October.† It is, therefore, the meteorological conditions on the Abyssinian plateau which determine the rainfall which supplies the whole of the annual flood of the Nile.

A discussion of all available data concerning the Abyssinian rainfall‡ shows that the distribution of rain in the different months of the summer is approximately as follows:—

	June.	July.	August.	September.
North of lat. 9° N....	15 per cent.	30 per cent.	30 per cent.	15 per cent.
South of lat. 9° N....	5 ,,	30 ,,	30 ,,	25 ,,

the remaining 10 per cent. falling in March, April, and May. As the flood wave caused by rainfall in the basin of the Abai or Blue Nile takes from 25 days in July to 15 days in September to reach Aswan,§ we may consider that the meteorological conditions which we have to examine are those of June, July, August, and September, the months of heaviest rainfall on the Abyssinian plateau.

Summer Pressure Anomalies and Flood Conditions.—If the yearly variations

* "Die Anomalien der Witterung auf Island in dem Zeitraume 1851 bis 1900 und deren Beziehungen zu den gleichzeitigen Witterungs-anomalien in Nordwest-Europa," 'Sitzungsberichte d. k. Akad. Wiss. in Wien,' 1904.

† Garstin, 'A Report on the Basin of the Upper Nile,' Cairo, 1904; also Blue-book, 'Egypt, No. 3, 1904;' Lyons, 'Geog. Journ.' (not yet printed).

‡ Lyons, 'The Climatography of the Nile Basin,' Survey Dept., Egypt (in the press).

§ Lyons, 'Geog. Journ.'

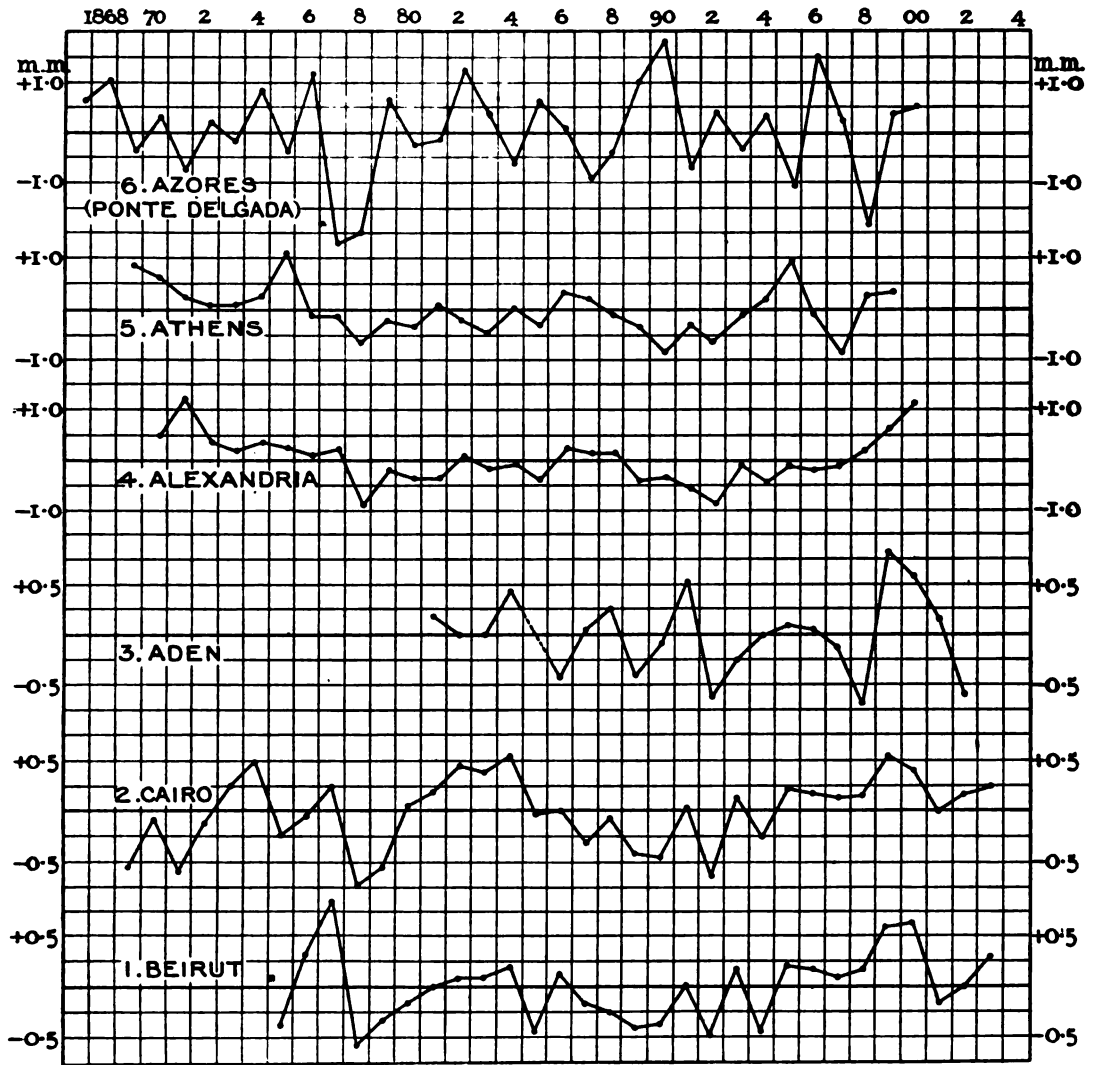
from the mean of the atmospheric pressure of the summer months, April to September, are examined (fig. 1), it will be seen that they exhibit an irregular oscillation which is generally inverse to that of the Nile floods; years with high atmospheric pressure correspond closely to those of deficient Nile floods, and those of low atmospheric pressure to the high floods, and consequently with heavier rainfall in Abyssinia. As has been shown by Brückner, Sir N. Lockyer, Bigelow, and others, such oscillations of pressure are to be traced over very wide areas, high or low pressures occurring at nearly the same time in the observations recorded at distant stations. The data which are available for an investigation of the pressure conditions occurring over the Nile basin itself are few, since temperature and rainfall have been more often recorded than atmospheric pressure, for which only a few years' observations in the Nile valley, south of Cairo, and in the Sudan exist as yet; still the observations which are available at Cairo and Alexandria from 1869, and Beirut from 1875, may be utilized to compare the pressure conditions of north-eastern Africa with those of more distant stations.

Taking, now, the summer or low pressure months, April to September, which include the period of rainfall in Abyssinia, the mean value of the barometric pressure is usually above the normal value for these months (as deduced from the 35 years, 1869 to 1903), when the Nile flood is below the average, and below it when the flood is above the average in this series of years (fig. 1); a mean atmospheric pressure for April to September in excess of the normal occurred with twelve low floods as compared with seven high floods, while a deficient mean pressure occurred with fourteen high floods and no low floods.

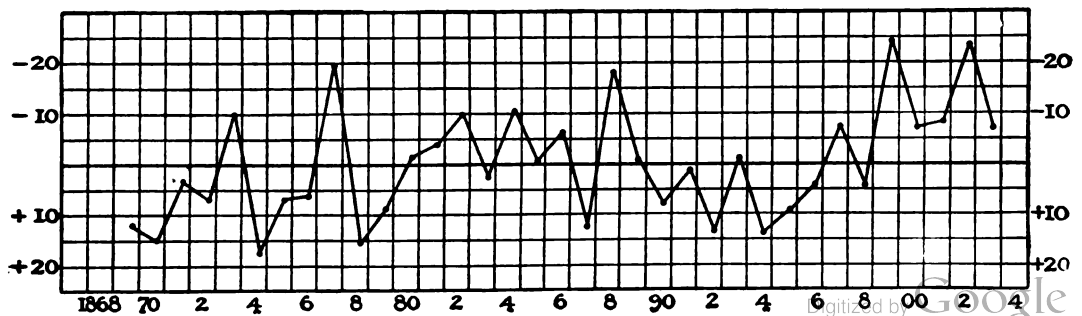
The agreement is more clearly shown if the curves of the mean pressure anomalies and of the Nile floods (inverted) are compared. It will then be seen that not only do excess pressures and deficient floods, and the converse, occur with considerable frequency, but also that the differences from the normal of the two curves, as plotted on fig. 1, show a marked tendency to move in the same direction, although the amount of excess or deficit for any year in the atmospheric pressure may not bear any definite relation to the magnitude of the flood. Of 18 years, in which there was an increase in the mean pressure of April to September, there was a decrease in the flood as compared with the previous year in 16 years and in 2 years there was an increase; in 14 years, in which there was a decrease in the barometric pressure as compared with the previous year, 9 years had an improved flood and 5 years had a worse flood. Therefore, though there is not an exact agreement between the curve of the mean atmospheric pressure for April to

FIG. 1.

Mean Variation of Atmospheric Pressure from Normal for the Months April-September.



Curve (inverted) of Nile Flood.



September at Cairo, and the inverted curve of the Nile floods, there is considerable similarity, which is worth further investigation.

The years in which the agreement is wanting, when the mean summer pressure for April to September and the flood are compared, are :—

	Pressure difference from pre- ceding year.	Pressure difference from normal.	Flood difference in volume from previous year.*	Flood difference from mean.*
	mm.	mm.	Million cubic metres.	Million cubic metres.
1871	- 0·49	- 0·59	- 11,800	+ 3,184
1872	+ 0·44	- 0·15	+ 3,700	+ 6,877
1874	+ 0·29	+ 0·55	+ 27,600	+ 17,434
1875	- 0·79	- 0·24	- 10,700	+ 6,709
1886	+ 0·05	+ 0·01	- 5,320	- 5,855
1901	- 0·42	0·00	- 1,500	- 8,661

If the investigation is carried out over a wider field, and the records of barometric pressure of other and more distant stations are utilised, this general agreement is seen to extend to many of them, also showing that variations from the normal pressure occur nearly simultaneously over very large areas.† The variations from the normal pressure have been plotted on Plate 1 for the stations of

Beirut.	Zanzibar.	Bombay.
Cairo.	Mauritius.	Hong-Kong.
Aden.	Bushire.	Shanghai.

Here the general agreement of the maxima and minima are well shown, as well as many of the minor crests, so that it would appear that the barometric conditions, with which a heavy or deficient rainfall in Abyssinia coincides, are often of very wide extension. The agreement of the Cairo pressure curve with the inverted flood curve has been discussed; the Beirut curve has much in common with the Cairo curve but presents some points of interest; the high pressure in 1877 is well marked, coinciding with the very low Nile of

* The volume of the flood is taken as the volume of water passing Aswan between July 1 and October 31.

† See Lockyer, 'Roy. Soc. Proc.,' vol. 73, p. 457; Bigelow, 'Monthly Weather Review,' November, 1903; Brückner, 'Klimaschwankungen,' Chap. VI, Vienna, 1890; Hann, 'Sitzungsberichte d. k. Akad. d. Wiss. in Wien,' vol. 110, III, January, 1904.

that year, as it is in the Bombay and Mauritius curves; at Cairo the discrepancy between the two curves is apparent rather than real, as the pressure was exceptionally high in July and August.

All the curves mark the low pressure of the summer of 1878, a year of high and late flood. In 1879 the pressure was rather higher but agrees with the flood; 1880 continues in the same direction, as also does 1881. In 1882 there are points of peculiar interest to be noted; at Cairo, Beirut, and to a lesser degree at Bushire, the mean pressure increased, and in Egypt the Nile flood was feebler than in any year since 1877, these data being thus in agreement; but in Mauritius, Aden, and Bombay the pressure fell considerably, the Bombay rainfall was in slight deficit, -1.92 inches, while that for India generally from June to September was 2.1 inches above normal. In 1883 a marked improvement in the flood took place, with a very slight decrease of pressure at Cairo, Beirut, Aden, and rather more at Bushire, but at Bombay it rose. In these two years then Indian and Egyptian pressures and rainfall conditions were not in agreement. In 1884 again the mean pressure increased at most stations and the Nile flood was bad; in 1885 the mean pressure fell at Cairo, Beirut and Aden, it rose at Bushire and Bombay the Nile flood was slightly above the average again, while in Bombay rainfall was 3.1 inches below the average; 1886 shows rather higher pressures at Cairo and Beirut, while the flood was poorer, but Aden, Bushire, and Bombay had lower pressures, and at Bombay there was a large excess of rainfall; in 1887 the conditions were reversed except that in spite of increased pressure Bombay had an excess of rainfall, but the noticeable point is that in these two years again, as in 1882 and 1883, Egypt and Western India are at variance. In 1888, 1889, and 1890 all the curves agree except Aden in the latter year, and the very low flood of 1888 followed by higher ones of 1889 and 1890 are paralleled by the failure of rainfall at Bombay in the first year, and the greatly reduced deficits of the next two years. Until 1894 the curves show satisfactory agreement, but in that year Aden and Bushire contradict the others; in 1895 agreement is again general, but in 1896, 1897, and 1898 the variations of the flood are not well indicated in the Cairo and Beirut curves, and in 1897 Zanzibar alone shows an increased mean pressure.

Pressure Anomalies in the Mediterranean.—In the Mediterranean area the pressure anomalies in summer are generally of the same character as those of Cairo and Beirut, as is shown by the curves of Athens and Palermo, but those of the Azores (Ponte Degada) and Lisbon are usually inverse. It is instructive to notice that in the years 1871, 1874, 1881, and 1882, the Egyptian pressures differ markedly from those of Bombay and India

generally, but they agree closely with those of the Azores (see fig. 1), that is with the indirect or Cordoba type of pressure variation, which seems in these years to have extended across northern Africa to Cairo. In 1874 the flood was a very high one, which would not have been anticipated from the high pressure at Cairo, although the pressure fell much in July; possibly conditions to the southward were more favourable than the Mediterranean stations indicate, but no observations are available to bear this out. We find then that Egypt and Abyssinia in their pressure anomalies in the summer months usually agree with the Indian or direct type of pressure, but occasionally revert for a year or two to the opposite type.

Monthly Pressure Anomalies.—So far then, there appears to be considerable probability that the variations of the rainfall in Abyssinia are connected with the variations of barometric pressure from year to year in north-eastern Africa in the summer months, that is from April to September; but it must be remembered that in taking the mean pressure for the six months, April to September, the first two months are unimportant, since practically no rain then falls which appreciably affects the flood, and meteorological conditions in these months may be highly favourable or unfavourable to precipitation without any material effect being produced on the Nile flood, though the mean pressure for the six months is affected by them. It may be to this and to the fact that two or three stations only can furnish observations which are of use in this discussion, that the discrepancies which have been pointed out are due.

When the monthly pressure anomalies at Cairo, Alexandria and Beirut are compared with the monthly excess or defect of the Nile flood as recorded on the Aswan gauge, a closer agreement is found to exist. Sir J. Eliot, F.R.S.,* points out that periodic changes of pressure in India are far smaller in amount than the annual and daily range, take place more gradually, and from their small magnitude accurate and long-continued series of observations are necessary for their discussion. Their importance is not, however, to be measured by their size; Sir J. Eliot is of opinion that in India they are due to the seasonal mass transfer of air across the equatorial belt between Southern Asia and the Indian Ocean and, as a consequence of this, "they are directly related to the largest and most important features of the weather in India, viz., the character and distribution of the precipitation of rain and snow in the Indian monsoon area.† It will hardly be remarkable if a somewhat similar oscillation be found to exist in the north-eastern part of Africa, and

* 'Indian Meteorological Memoirs,' vol. 6, Part II, Calcutta, 1895.

† *Ibid.*, p. 117.

we may expect it similarly to affect the African monsoon rainfall in Abyssinia and the Sudan.

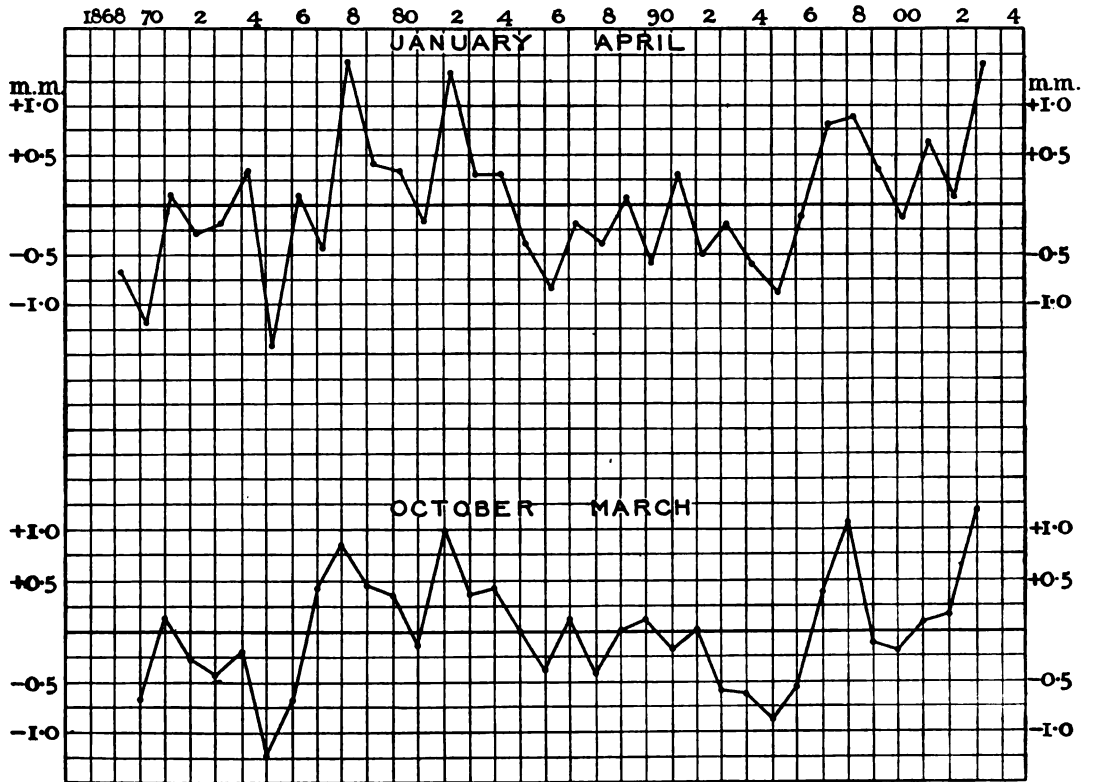
To examine this the "smoothed" values of the differences of mean atmospheric pressure of each month from the normal for Abbassia Observatory, Cairo, have been used. The smoothed values are obtained in the same way as in the Indian Meteorological Memoir already quoted, that is, the smoothed values for any month is the arithmetical mean between the actual values for that month, the preceding and succeeding months. The same has also been done for Beirut, Aden, Zanzibar and Mauritius, and for India, for which the figures have been taken from Sir J. Eliot's Memoir. These smoothed values have been plotted on Plate 1 to a scale of 5 mm. to 1 mm. of variation of pressure from the normal, so that the correspondence between the various stations at the same season can be followed. In the Indian Memoir, (Vol. 6, pt. II) freehand curves have been drawn through the Indian curves; this could easily be done for the Zanzibar curve, but those of Beirut and Cairo are too irregular for a satisfactory curve to be drawn, though traces of oscillations similar to the Zanzibar curve can be traced here and there in them.

In studying these curves, and especially those of Beirut, Cairo, and Aden, we must remember that it is with the effect of the pressure variation during June, July, August, and September that we are principally concerned. This leads to another point; since the rainfall which affects the Nile flood is strictly limited to the Abyssinian area, high and low pressures may occur in the winter months without having any effect on the subject under consideration, the Nile flood. This is the reason that if the mean pressures at Cairo for October to March or even January to April are examined, they show no relation to the variations of the Nile flood (fig. 2).

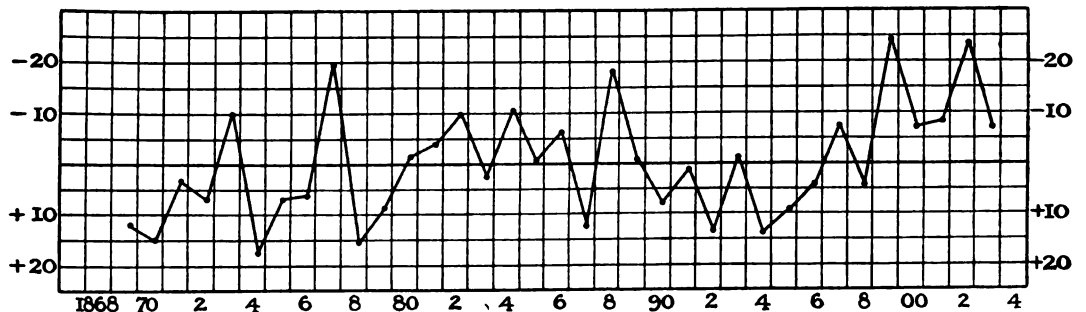
Flood Conditions.—The agreement between the barometric curve for Cairo and the variation of the Abyssinian rainfall and the Nile flood, cannot conveniently be shown graphically when the monthly pressure variations are considered, because the discharge of the Nile in different months depends on different factors. After October the Blue Nile supplies a steadily decreasing amount, until in May its discharge at Khartoum may almost cease; the Sobat is at its maximum in November and decreases until it, too, supplies hardly anything in April in a low year; the combined discharge of the Bahr-el-Zaraf, Bahr-el-Jebel and Bahr-el-Ghazal is always a practically constant amount for the purpose of the present discussion. Although, therefore, pressure conditions might be such in November as to favour a heavy rainfall, and even though this might fall at the equatorial lakes, the Nile discharge would no more be

FIG. 2.

Mean Variation of Atmospheric Pressure from Normal at Cairo.



Curve (inverted) of Nile Flood.



influenced by it than by conditions of excessive drought at a similar time. In short, conditions favourable or unfavourable to precipitation will affect the Nile flood supply in some such way as the following:—

April and May: Advance or retard commencement of flood; June, July,

August: Increase or decrease flood; September, October: Delay or accelerate the fall of the flood.

In other months they will have no effect on the Nile supply, since no rain is falling within the effective basin.* The low-stage supply is due to the combined effect of the July to August rainfall, and to the September to October later rains; a heavy rainy season ceasing usually in September, and a moderate rainy season, followed by prolonged September to October rains, may both furnish a good low-stage supply drawn from the stored ground-water and the springs of Abyssinia.

Since the pressure changes are practically simultaneous over wide areas, their effect on the river gauge readings will take place in the flood two to four weeks later at Aswan, according to the distance that the water has to flow, from where the rain was falling to the point of observation, and also on the velocity of the current, while at low stage the discharge is the result of the meteorological conditions in Abyssinia several months earlier. Since, therefore, the pressure curves and river gauge curves cannot be directly compared, Table I, which gives the mean difference of each month's gauge readings from the 32 years' mean of the readings of the Aswan gauge, will be used to show the effect of the rainfall on the river's discharge.

Comparison of Monthly Pressure Anomalies with Excess or Deficiency of Flood.—A comparison of these differences with the pressure anomalies on fig. 1, will serve to show the remarkably close connection which there is in most years between the variations of pressure from the normal at Beirut, Cairo and Aden, and the rainfall of Abyssinia, as represented by the gauge readings at Aswan. In one or two cases even a brief change of pressure for a month appears to be reproduced in the gauge readings, as a consequence of the increased or decreased rainfall, but though no special stress should be laid on these minor agreements, it is certainly remarkable to see how closely the two phenomena of pressure and rainfall agree in most years.

The following table (No. I) gives the monthly mean difference of the Aswan gauge readings from the mean readings of 1872 to 1901, and though these differences do not furnish as accurate a means of comparison as the volume of water discharged in each month would do, still they will not introduce any great error. In Table II the pressure anomalies for June to September are compared with the flood for the year by means of its ratio

* Strictly speaking, Wadelai on the Bahr-el-Jebel (lat. 3° N.), which has November rains, would be within the effective basin, since there is a direct waterway from this point to the lower reaches of the Nile, but as the discharge at the mouth of this river, where it joins the White Nile, only varies between 250 and 350 cubic metres per second throughout the year, this rainfall has no seasonal effect on the Aswan discharges.

to a mean flood. This ratio has been obtained by comparing the volume discharged at Aswan between July 1 and October 31 in each year.

The nine years which disagree may now be examined more in detail.

In 1874, pressure at Cairo was much above the normal in March, April, and May, after which it fell rapidly till the end of the year; the flood at Aswan was in considerable excess from the middle of June onwards.

In 1876, though Cairo pressure was above the normal, that of Beirut and Alexandria was below it.

Table I.—Mean Difference of Gauge Readings at Aswan in Centimetres from the Mean Gauge Readings of 1872 to 1901.

Year.	July.	Aug.	Sept.	Oct.	Year.	July.	Aug.	Sept.	Oct.
1869	+ 46*	+ 39	+ 61	+ 115	1887	+ 79	+ 122	+ 77	+ 14
1870	+ 71	+ 108	+ 53	+ 95	1888	- 82	- 74	- 106	- 146
1871	+ 32	+ 57	+ 22	+ 1	1889	- 61	+ 14	+ 23	+ 4
1872	+ 88	+ 42	+ 34	+ 78	1890	- 13	+ 74	+ 46	+ 80
1873	+ 18	- 58	- 48	- 54	1891	- 5	+ 6	+ 15	+ 48
1874	+ 76	+ 124	+ 94	+ 83	1892	- 30	+ 40	+ 99	+ 121
1875	+ 13	+ 58	+ 36	+ 64	1893	- 54	+ 20	- 22	+ 51
1876	+ 93	+ 42	+ 63	+ 11	1894	+ 65	+ 72	+ 68	+ 131
1877	+ 47	- 107	- 154	- 122	1895	+ 62	+ 144	+ 41	+ 1
1878	- 24	+ 10	+ 95	+ 182	1896	+ 38	+ 2	+ 53	+ 29
1879	+ 168	+ 72	+ 44	+ 42	1897	+ 2	- 56	- 16	- 26
1880	+ 122	+ 27	- 24	- 18	1898	- 47	+ 42	+ 42	+ 55
1881	- 44	- 78	+ 28	+ 2	1899	- 52	- 144	- 152	- 194
1882	- 92	- 80	- 34	- 45	1900	- 105	- 17	- 55	- 41
1883	+ 43	+ 55	+ 22	- 3	1901	- 30	- 16	- 23	- 105
1884	- 45	- 75	- 62	- 10	1902	- 120	- 249	- 127	- 79
1885	+ 78	+ 66	- 28	- 39	1903	- 49	- 118	- 18	+ 10
1886	- 38	- 12	- 2	- 41					

In 1883, pressure was above the normal until October, the maximum being in July; the flood was in moderate excess July to September, with a considerable excess July 25 to August 10; October in moderate defect.

In 1888, pressure at Cairo was below normal till August, then above it; Beirut was below normal, but rising; at Aden it was high in September. The flood of July and August was in considerable defect, and after September 15 in large defect.

In 1891 pressure at Cairo was below normal April to June, and above it July to September; pressure at Aden fell steadily after July. The flood was

* Ten days only.

in good excess June 10 to July 5, moderate defect July 15 to August 10, normal July 20 to September 30, moderate excess in October.

In 1893, pressure at Cairo was high in March, April, and May, after which it fell to slightly below normal; at Beirut July was above normal, after which pressure fell; at Aden pressure rose in August. The flood was in defect in June and July; in fair to good excess in August; in moderate defect in September.

In 1895 pressure at Cairo was high in April to June, after which it fell

Table II.—Comparison of Pressure Anomalies, June to September, at Cairo, with the Ratios of the Nile Floods to a Mean Flood.

Year.	Ratio to mean flood.	Pressure anomaly.*	Year.	Ratio to mean flood.	Pressure anomaly.*
		mm.			mm.
1869	1.18	-0.67	1887	1.19	-0.47
1870	1.23	-0.12	1888	0.72	-0.06†
1871	1.05	-0.49	1889	1.00	-0.45
1872	1.11	-0.49	1890	1.12	-0.28
1873	0.84	+0.43	1891	1.01	+0.42†
1874	1.26	+0.36†	1892	1.20	-0.52
1875	1.10	-0.14	1893	0.99	-0.22†
1876	1.09	+0.16†	1894	1.22	-0.38
1877	0.70	+0.91	1895	1.15	+0.33†
1878	1.25	-0.86	1896	1.06	+0.09†
1879	1.14	-1.15	1897	0.89	+0.06
1880	0.98	+0.11	1898	1.07	-0.005
1881	0.93	+0.11	1899	0.63	+0.54
1882	0.84	+0.60	1900	0.89	+0.30
1883	1.04	+0.39†	1901	0.87	-0.09†
1884	0.83	+0.95	1902	0.63	+0.11
1885	0.99	+0.02	1903	0.89	+0.30
1886	0.91	+0.17			

steadily, being normal in August; at Aden it was low after June. The flood was in good excess June to September, and in large excess August 1 to 25.

In 1896, pressure at Cairo was high June to August, and low in September; at Aden generally low but above normal in August. The flood was in small excess in June, moderate excess in July, considerable defect in August, and good excess in September.

* Mean of the mean anomalies of the months June, July, August, September.

† Years in apparent disagreement from the rule that - anomalies coincide with floods above the average, and + anomalies with floods below the average.

In 1901, pressure at Cairo was high till May, then fell to just below normal; Aden and Zanzibar were above normal. The flood was in moderate defect until the end of September, except for a moderate excess from August 15 to 31; in October there was a large defect.

Out of these nine years then, 1883 and 1895 floods alone are in disagreement, while those of 1874 and 1896 are in fair agreement only, though it should be said that the years of 1888 and 1902 were not so remarkable for conditions of high pressure as the deficiency of rainfall would have led one to expect.

Percentage of Agreement.—Still we may say that 30 out of the 35 years, or 86 per cent., show a good agreement of — anomalies of pressure with excess of rainfall and + anomalies with a deficiency, which is sufficiently satisfactory to encourage further study; it at all events furnishes a working hypothesis which may be used to estimate the probability of a year's flood being much below or above the normal, and as knowledge advances a closer estimate may perhaps be formed.

Extent of Agreement with the South-west Monsoon of India.—As the Abyssinian rains are due to the monsoon of Eastern Africa, which in the summer months crosses the equator and extends as southerly and south-westerly moisture-laden winds as far as Khartoum (lat. $15^{\circ} 40' N.$), and even to Suakin (lat. $19^{\circ} N.$), it is not surprising that there should often be considerable similarity between the Abyssinian rainfall and the south-west monsoon of India. The relation is not, however, so close as Sir W. Willcocks* and Sir John Eliot† have maintained; years of famine or excessive rain in India usually coincide with low or high Nile floods as might be expected, since conditions unfavourable or favourable to precipitation will be strongly marked and consequently wide in their influence,‡ but if the series of years, 1875 to 1903, is taken, 9 years§ out of 27 are in disagreement, as may be seen from the following table. If the Bombay rainfall is taken, the result is even less satisfactory. Therefore, in basing anticipations of the Nile flood solely on the prospects of the Indian south-west monsoon, it would seem likely that as many times as 1 in 3 they would not be fulfilled, a very much lower proportion than the 1 in 7, derived from the barometric anomalies of Beirut, Cairo, and Aden.

Low Stage of Nile.—Besides the heavy rains of July and August which

* A paper read before Meteor. Congress, Chicago.

† 'Nature,' August 23, 1900, p. 392.

‡ Lyons, 'Geog. Journ.'

§ *I.e.*, 1876, 1881, 1882, 1883, 1884, 1886, 1891, 1896.

Table III.

Year.	Ratio of Nile flood to mean flood.	Indian rainfall.* Year variation from normal.		Bombay rainfall.† Variation from normal. April to September.
		Year.	June to Sept.	
		in.	in.	in.
1875	1·11	+2·38	?	+13·08
1876	1·10	-4·49	-3·4	-21·00
1877	0·71	-4·28	-9·3	+1·40
1878	1·25	+6·34	+2·9	+41·71
1879	1·15	+1·69	+2·7	-9·64
1880	0·99	-1·56	-2·6	-3·10
1881	0·64	+0·10	+2·4	+1·99
1882	0·65	+2·64	+2·1	-1·92
1883	1·05	-0·12	-1·7	+19·05
1884	0·84	+1·73	+2·5	+3·26
1885	1·00	+1·05	+0·8	-3·10
1886	0·92	+3·02	+1·4	+28·72
1887	1·21	+2·42	+0·1	+23·76
1888	0·72	-1·54	+0·6	-15·16
1889	1·00	+2·41	+3·3	-3·26
1890	1·13	+0·68	+1·3	-5·97
			June to Dec.	
1891	1·02	-3·54	-4·25	+5·94
1892	1·21	+5·09	+5·69	+24·10
1893	1·00	+9·07	+4·72	-4·13
1894	1·23	+6·47	+6·75	-4·46
1895	1·16	-2·90	-1·95	-3·49
1896	1·08	-4·83	-3·59	+16·63
1897	0·90	-0·15	-0·02	+10·51
1898	1·07	+0·43	+0·93	+2·91
1899	0·63	-11·14	-11·34	-36·68
1900	0·90	-0·57	-0·26	-1·87
1901	0·88	-4·13	-5·12	
1902	0·64	-2·05	-1·64	
1903	0·89			

principally supply the Nile flood, the meteorological phenomena may also indicate conditions favourable or unfavourable to precipitation at the time of the later autumn rains of September and October which affect the low stage or summer supply of the river.

* Eliot, 1875 to 1896, see 'Nature,' June 3, 1897, p. 110; 1897 to 1902, see 'Nature,' August 25, 1904, p. 403.

† 'Indian Meteorological Memoirs.'

The connection is not so simple as in the case of the flood, for the effect of heavy autumn rains may be counteracted by the effects of a very deficient rainfall of earlier months, while an unusually copious rainfall will give a good low stage supply, even though the autumn rains have been feeble.

In Table IV the pressure anomalies for September and October are compared with the mean excess or defect of the March to May gauge readings at Aswan of the following year. From this it is seen that out of 34 years a negative value of the mean of the anomalies for September and October was followed by a low stage above the average, and a positive value by one below the average in seventeen cases.

If now we take the excessively high floods of 1870 and 1878, when the summer rains were sufficiently heavy to mask any effect of the positive pressure anomalies in the autumn, and also the very low floods of 1873, 1877, 1888, 1901 and 1902, when deficient summer rainfall outweighed the precipitation which we may assume accompanied the small negative pressure anomalies of the autumn, the cases which agree with what might be expected are 24 out of 34, or 71 per cent.; of the 11 discrepant years, 1871 and 1891, which were followed by a deficient low-stage supply, and 1883, which was followed by a favourable low stage, had respectively + and - pressure anomalies in September, which month would naturally be more effective in rainfall than October.

This agreement is as good a one as can be expected where so many causes are at work, and where no data from the immediate neighbourhood are available.

It should be mentioned here that the true distribution of pressure in Egypt and the Sudan is very different from that usually shown in meteorological atlases.* In April and May the principal feature is a low-pressure area which lies over Abyssinia and the Eastern Sudan, and to which the early rains (Azmera) of Abyssinia are due; by June it has joined the trough of low pressure which extends across Beluchistan in a south-westerly direction, and a gradient exists everywhere from the Nile Valley towards the neighbourhood of Muskat and Bushire. In July this gradient is steepest; in August it is somewhat reduced by a slight rise of pressure in the Persian Gulf, and is very considerably reduced in September. Thus instead of a continuous trough of low pressure extending from Central Asia into the central part of North Africa, there is a marked gradient† eastwards

* This distribution of pressure is discussed in a Report on the Climatology of the Nile Basin which will be published shortly.

† Five millimetres in about 8° of longitude between Dueim, lat. 14° N. on the White Nile, and the Red Sea in July.

Table IV.

Year.	Pressure variation.			Flood ratio to mean flood.	Mean difference from mean gauge readings at Aswan, of March, April, May, next year.
	September.	October.	Mean.		
	mm.	mm.	mm.		cm.
1869	-1.16	+0.75	-0.20	1.18	—
1870	+0.04	+0.15	+0.10	1.23	+ 39
1871	+0.34	-0.65	-0.16	1.05	- 52
1872	+0.34	+0.15	+0.25	1.11	- 2
1873	-0.36	+0.05	-0.16	0.84	- 79
1874	+0.44	+0.35	+0.40	1.26	- 4
1875	+0.84	-3.05	-1.10	1.10	+ 39
1876	+0.34	+0.45	+0.40	1.09	- 4
1877	-0.26	-0.45	-0.36	0.70	- 74
1878	-0.38	+0.47	+0.05	1.24	+177
1879	-1.11	+0.52	-0.28	1.14	+110
1880	+0.14	+0.27	+0.20	0.98	- 6
1881	-0.03	+0.06	+0.02	0.93	- 35
1882	+0.38	+0.37	+0.38	0.84	+ 20
1883	-0.45	+0.68	+0.12	1.04	+ 58
1884	+0.98	+0.68	+0.83	0.83	- 25
1885	+0.08	+0.19	+0.14	0.99	- 26
1886	-0.11	-0.52	-0.32	0.91	- 21
1887	-0.21	-0.58	-0.40	1.19	- 10
1888	+0.42	-0.45	-0.02	0.72	- 82
1889	-0.28	+0.25	-0.02	1.00	- 67
1890	+1.44	+0.97	+1.20	1.12	- 32
1891	+0.68	-0.77	-0.04	1.01	- 48
1892	-0.80	-0.61	-0.70	1.20	+123
1893	-0.68	-0.25	-0.46	0.99	- 15
1894	-0.40	+0.27	-0.06	1.22	+104
1895	+0.92	-0.87	+0.02	1.15	+ 58
1896	-0.54	-0.02	-0.28	1.06	+ 66
1897	-0.17	+0.92	+0.38	0.89	- 25
1898	-0.17	-1.30	-0.74	1.07	-129
1899	+0.11	+0.31	+0.21	0.63	+ 72
1900	+0.69	+0.28	+0.48	0.89	- 61
1901	-0.07	-0.18	-0.12	0.87	- 76
1902	-0.39	+0.30	-0.05	0.63	- 85

from about the line of the Nile Valley. Here the isobars run from N.N.W. to S.S.E. as far as about lat. 10° N., when they turn E.S.E.

The last few years have shown that the rainfall on the Bahr-el-Jebel, lat. 2° N. to lat. 7° N., may differ entirely from that of Abyssinia in its

character, but the causes of this are still unknown. In 1878 and 1879 the rainfall was exceptionally heavy in both areas; in 1899 it was extremely deficient in both; on the other hand, while 1902 and 1903 were years of very deficient and slightly deficient rainfall in Abyssinia, the fall in the districts to the north of Lake Albert was very heavy and exceptionally heavy respectively.

Possibility of Flood Prediction.—The present hypothesis seems to furnish us with a more satisfactory basis for predicting the character of the Nile floods when it is used in conjunction with the indications of the Indian south-west monsoon, as they are construed by the Meteorological Department of India, than most of the proposals which have been previously made.

Mahmud Pasha El Falaki, in a paper* read before the Khedivial Geographical Society at Cairo, January 6, 1882, suggested that the Nile flood might be predicted by a study of the temperatures and barometric pressures observed at Cairo, and as he was under the impression that the White Nile furnished a considerable part of the flood, he proposed to consider the meteorological conditions in February, March, and April as furnishing a guide to the probability of an excess or deficit of equatorial rainfall, and those of July as indicating the conditions on the Abyssinian plateau. Having taken the spring months, he was led to consider that a high temperature and a low pressure coincided with the low flood, and a low temperature and high pressure with a high flood, basing his view on the years 1870 to 1881.

Ventre Pasha,† in a paper on the hydrology of the Nile, discusses the possibility of predicting the flood, and concludes that the knowledge of the force and direction of the winds in the neighbourhood of Aden and Zanzibar should furnish a basis for satisfactory forecasting. He refers to some investigators who have endeavoured to trace a connection between the Nile flood and the barometric pressure and temperature at Cairo, but that such a relation is possible he denies, apparently on the ground that the distance between the equatorial lakes and Cairo is over 3500 kilometres, and consequently too great for meteorological phenomena at the two places to have any relation to one another; but it is with the Abyssinian plateau some 2200 kilometres distant that we have to do, and also variations of barometric pressure are frequently found to occur over as great and even greater areas.

Ventre Pasha also speaks of what he considers to be a law,‡ viz., that a

* 'Bull. Soc. Khéd. Géog.,' February 6, 1885, p. 327.

† 'Bull. Soc. Khéd. Géog.,' January, 1894, Cairo.

‡ 'Bull. Soc. Géog. Cairo,' January, 1894, p. 41.

low flood is followed by a low summer supply, but this is only a natural sequence, since a low flood means insufficient rainfall on the Abyssinian area, and consequently the September rains are likely to be also below the average. Therefore the springs and streams will run low or dry sooner than in wetter years, and the Sobat and Blue Nile, the two variable factors of the summer or low-stage supply, will be furnishing but little. On the other hand, it will sometimes occur that a season of deficient rainfall may improve towards the end, as was the case in 1903, when the increased rainfall in the autumn provided a good low-stage supply for 1904.

It is, therefore, rather on the amount of rain falling at the end of the rainy season in Abyssinia, and its continuance into the autumn months, that a good low-stage supply depends; the Sobat keeps up the level of the White Nile with the water it brings from the high lands of Kaffa, and the Blue Nile is fed by its tributaries in Gojam and Wallega. In 1903, the Blue Nile was discharging nothing at Khartoum on the 8th, 15th, and 23rd of May, after the deficient rainfall of 1902.

Sir W. Willcocks,* in his paper on the Wadi Rayan, refers incidentally to the prediction of the Nile floods, and considers that good floods coincide with high humidity in June, and with a prevalence of southerly winds in April and May at Cairo; also that deficient floods are heralded by exceptional dryness in June and few southerly winds in April and May.

In the 33 years—1870 to 1902—the mean relative humidity in June is not of any real value as a guide in prediction, since out of 19 years in which the relative humidity in June was above the mean, 9 floods were below the average, and 10 were above it; and of 13 years in which the humidity was below the mean, 8 floods were above the average, and 5 were below it.

Turning now to the southerly winds, the number of observed winds of which the direction was south of east or west (from some part, that is, of the southern half of the horizon) has been taken from the 3-hourly observations at Abbassia (near Cairo). In 9 years, when the flood was above the average, the southerly winds were above the average in 5 years, and below it in 4 years. In 7 years having floods *below* the average the southerly winds were below the average in 4 years and above it in 3 years.

It cannot therefore be said that either the mean relative humidity in June or the prevalence of southerly winds in April and May are safe guides in predicting the Nile flood; the proposed relation will be found to hold

* 'The Aswan Reservoir and Lake Moeris,' London, 1904; and 'Khéd. Géog. Soc.,' January, 1904.

occasionally, as in 1902, when there were few southerly winds and a large deficiency in the flood, also in 1892 was a high Nile, and the June relative humidity was also high, but in no sense can they be considered as satisfactory bases for regular prediction. Sir W. Willcocks does not say what he considers the relation between these phenomena, and the precipitation in Abyssinia to be; no relation of cause and effect is indicated, nor are they shown to be effects of the same cause.

It seems that the two principal factors to be considered are firstly the strength of the south-east trade winds as they progress from the south to the north of the equator, along the eastern coast of Africa, and secondly, the excess or defect of atmospheric pressure in the area represented by Aden, Cairo, Beirut, and careful study, year by year, of the varying conditions, will be necessary before their effects are properly understood.

The results may be summarised as follows:—

1. Generally speaking the curve of Nile floods varies inversely as the mean barometric pressure of the summer months, high pressures accompany low floods, and low pressures accompany high floods.

2. These pressure variations show a great similarity over wide areas, from Beirut to Mauritius, and from Cairo to Hong-Kong, and are usually of Sir N. Lockyer's Indian type of curve, or Professor Bigelow's "direct" type.

3. Occasionally, however, pressure at Beirut and Cairo is in disagreement with that of the rest of the area, and then more nearly approaches the "Cordoba" type of Sir N. Lockyer, or the "indirect" type of Professor Bigelow. This would seem to be a confirmation of other evidence which tends to show that Egypt belongs to the class of Brückner's "temporarily exceptional" areas.

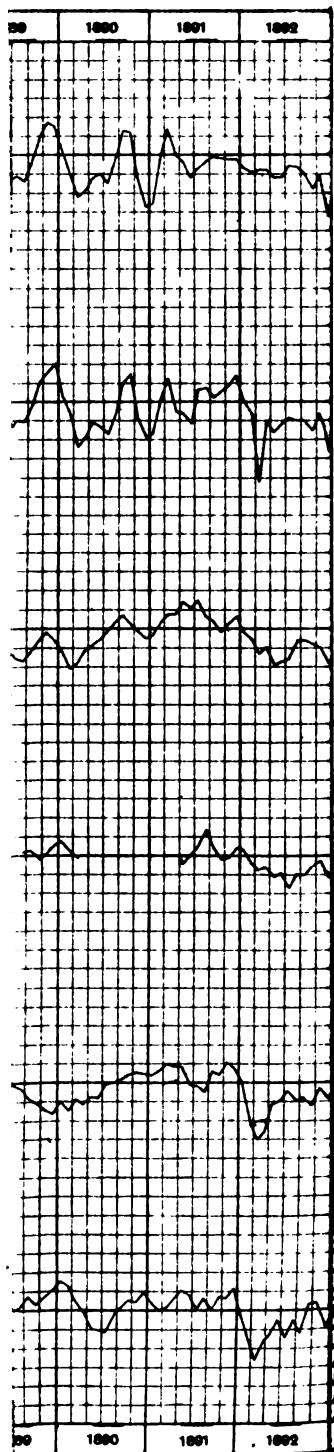
4. Taking the monthly means of atmospheric pressure, this relation is even more clearly shown, and pressure above or below the normal in months of the rainy season of Abyssinia coincides closely with deficiency or excess of rainfall.

5. Taking the 35 years—1869 to 1903—in 6 years out of 7 a very fairly accurate prediction of the flood from month to month could have been made.

Conditions in 1904. The data which have been utilised extend up to 1902 or 1903; 1904 may be examined to see what amount of accuracy would have been arrived at. In the early summer of the present year it was the general opinion in Egypt that there would be a good Nile flood, and Sir W. Willcocks wrote,* "Egypt has had a very good supply this year the Atbara and the other rivers are coming down fairly early, so that all anxiety about

* 'Egyptian Gazette,' June 11, 1904.

MONTHLY VALUES.



want of water may be dismissed for 12 months"; yet the flood of 1904 was a low one, and the low-stage supply promises to be exceptionally low. Looking at the meteorological data, at no time after April was there any evidence that the Abyssinian rainfall was likely to be heavy.

The following Table V shows that in Northern Egypt and Arabia pressure was in excess in April and May, and in June all stations show the same; by this time the slight deficiency in the river level at Wadi Halfa* in April and May had disappeared, but the high pressure in June rendered it improbable that the rainfall of that month in Abyssinia, which would affect the Nile at Wadi Halfa in July, would be above the average. In July, conditions were more favourable, and rains were plentiful, but in August, high pressure again set in, and in Abyssinia rains were very scanty, so that the mean level of the river at Wadi Halfa, was 83 cm. below the average in September.

In Table VI the mean 10-day readings of Roseires and Khartoum on the Blue Nile, and of Khashm-el-Girba and Berber for the Atbara, are given for 1903 and 1904. These show clearly that in June the river was low and rising slowly until the last week of June, when the level rose markedly, and this continued throughout July, until the beginning of August; then a rapid fall took place as the rains weakened in consequence of the unfavourable high pressure conditions, and as these continued throughout the month, it soon became clear that the flood would be a feeble one.

Table V.—Monthly Pressure Anomalies, 1904.

Place.	March.	April.	May.	June.	July.	Aug.	Sept.
	mm.	mm.	mm.	mm.	mm.	mm.	mm.
Beirut	-1·00	+0·30	+0·50	+0·33	+0·73	+0·66	+1·06
Alexandria	-1·00	+0·10	+1·00	-0·10	-0·70	+0·40	+0·70
†Aden	-0·80	-0·60	-0·30	+0·93	-0·23	+0·50	+0·88
Zanzibar	-0·43	0	-0·35	+0·66	-0·23	+0·45	+1·22
†Bushire	-0·70	+0·10	+0·80	+0·35	-0·45	-1·00	+0·82
†Muscat	-0·35	-0·65	-0·55	+0·23	-0·58	+0·23	+0·70
†Kuraachi	-0·30	-0·93	-0·73	+0·15	+0·08	+0·20	+1·80
Mauritius	-1·23	-0·10	+0·15	+1·55	+0·05		
Difference from mean of 1891 to 1902 in centimetres.							
Wadi Halfa Nile gauge	-17	-18	-7	0	-25	-42	-83

* The Aswan cannot be used, as in these months the reservoir is supplying water.

† After April taken from Daily Weather Reports.

Table VI.

	Roseires.			Khartoum.			Khaem-el-Girba.			Berber.		
	1904.		Diff.	1903.		Diff.	1903.		Diff.	1903.		Diff.
	m.	m.	m.	m.	m.	m.	m.	m.	m.	m.	m.	m.
May 1-10	-0.49	-0.26	+0.23	-0.23	0.12	+0.35	—	—	—	0.78	1.08	+0.30
" 11-20	0.06	0.06	-0.02	0.24	0.15	+0.39	—	—	—	0.78	1.00	+0.22
" 21-31	1.72	0.92	-0.80	0.39	0.38	-0.01	—	—	—	0.92	1.13	+0.21
June 1-10	2.08	1.49	-0.54	1.19	0.89	-0.30	10.94	9.88	-1.11	1.75	1.48	-0.27
" 11-20	2.12	1.27	-0.85	1.65	1.11	-0.54	11.21	10.40	-0.81	2.27	1.98	-0.29
" 21-30	2.10	2.46	+0.36	1.58	1.08	-0.50	12.05	11.12	-0.93	2.71	1.91	-0.80
July 1-10	3.18	3.65	+0.47	2.02	2.29	+0.27	12.32	12.23	-0.09	3.06	2.64	-0.41
" 11-20	3.96	4.42	+0.46	3.75	3.27	+0.52	12.41	13.00	+0.59	3.81	4.24	+0.43
" 21-31	4.80	6.02	+1.22	3.37	4.18	+0.81	12.85	13.50	+0.65	4.55	5.39	+0.84
August 1-10	7.37	7.52	+0.25	4.50	5.48	+0.98	13.52	13.96	+0.34	5.74	6.68	+0.94
" 11-20	8.42	6.08	-2.34	5.60	5.37	-0.23	14.94	13.01	-1.93	7.20	6.61	-0.59
" 21-31	8.29	6.55	-1.74	6.06	5.39	-0.67	14.69	13.07	-1.62	7.72	6.56	-1.16
September 1-10	7.88	6.42	-1.46	6.19	5.48	-0.71	14.51	12.98	-1.53	7.74	6.79	-0.95
" 11-20	7.24	6.88	-0.36	5.94	5.38	-0.56	13.98	12.58	-1.40	7.48	6.73	-0.75
" 21-30	6.85	5.24	-1.61	5.50	5.00	-0.50	13.25	11.84	-1.41	7.36	6.34	-1.02

With weak summer rains and high pressure conditions in September and the first part of October, no large amount of water can have been stored up in the soil of Abyssinia, so that the springs will run off early, and a very low stage may be expected in 1905.

Researches on some of the Physiological Processes of Green Leaves, with special Reference to the Interchange of Energy between the Leaf and its Surroundings. By HORACE T. BROWN, LL.D., F.R.S., and F. ESCOMBE.

On a New Method for the Determination of Atmospheric Carbon Dioxide, based on the Rate of its Absorption by a Free Surface of a Solution of Caustic Alkali. By HORACE T. BROWN, LL.D., F.R.S., and F. ESCOMBE.

On the Variations in the Amount of Carbon Dioxide in the Air of Kew during the Years 1898—1901. By HORACE T. BROWN, LL.D., F.R.S., and F. ESCOMBE.

On the Thermal Emissivity of a Green Leaf in Still and Moving Air. By HORACE T. BROWN, LL.D., F.R.S., and W. E. WILSON, D.Sc., F.R.S.

These papers, which formed the basis of the Bakerian Lecture, delivered by Dr. Horace T. Brown, on March 23, 1905, are published in Series B of 'Proceedings,' April, 1906.

On the Radio-active Minerals.

By the Hon. R. J. STRUTT, Fellow of Trinity College, Cambridge.

(Communicated by Lord Rayleigh, O.M., F.R.S. Received February 28,—Read
March 2, 1905.)

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Sec. 1.—*Introduction.*

As Professor Rutherford and Mr. Soddy have pointed out, the study of radio-active minerals is one of the most promising methods of attacking the problem of the connection between the radio-active elements, and the nature of the ultimate inactive products of their change. For in these substances we have, as it were, a laboratory in which the changes have been in progress for immense periods; there is, therefore, a fair chance of obtaining the ultimate products in measurable quantity. In many cases the life of a product is small in comparison with the age of the mineral. We may then expect to find it present in different minerals in a quantity proportional to the amount of its parent. In this way the connection can be made out. Finally, even when the changes are too slow for equilibrium to have been reached, the constant association of two substances may, none the less, give a valuable clue to their relative position in the series of radio-active products. The present paper is a contribution to this subject. It deals with the amount of uranium, radium, thorium, and helium in the minerals.

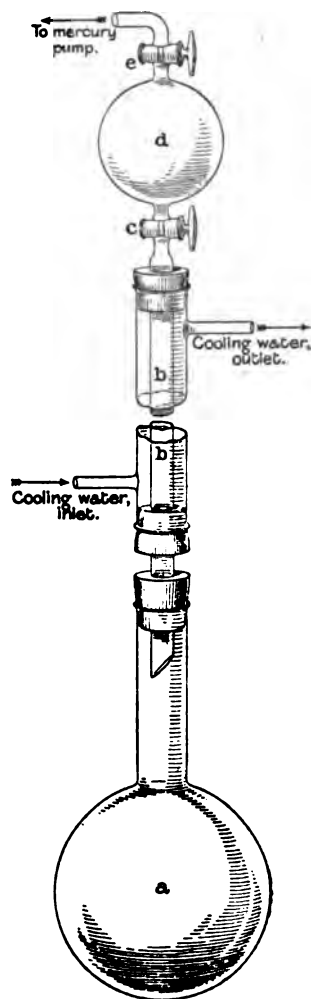
Sec. 2.—*Methods of Analysis.*

The uranium in the minerals was determined by the ordinary methods of chemical analysis. The majority of the analyses were made for me by Mr. Kitto, of 31, St. Swithin's Lane, E.C. Mr. H. J. H. Fenton, F.R.S., has also most kindly helped me with this part of the work.

The radium was determined by means of its emanation. A weighed portion of the mineral was decomposed, usually by fusion with borax to a clear glass. The residue was dissolved in dilute hydrochloric acid, in a small flask. The solution was boiled under a condenser for an hour, to thoroughly expel all radium emanation. The flask (*a* in the figure) was then attached airtight to the apparatus shown; *b* is an inverted condenser, communicating through the stop-cock, *c*, with the bulb, *d*. The latter, in its turn, communicates through a stop-cock, *e*, with a mercury pump, arranged for the collection of gas.

The flask was allowed to stand for a day; the quantity of emanation generated in that time measures the amount of radium present. In order to collect this emanation, the bulb, *d*, previously exhausted, and shut off from the pump, was placed in communication with the condenser, *b*, and the flask, *a*. The air previously in *a* and *b* partially flowed into *d*. In this way the pressure in *a* was reduced, and the liquid in it could be boiled without fear of generating excessive pressure inside. The emanation expelled by boiling mixed with the air in *a* and *b*. The liquid evaporated from *a* condensed in *b*, and ran back.

After the boiling had continued for an hour, the emanation was completely expelled. Test experiments have proved this. The flask, *a*, was then rapidly cooled with cold water; when cold, the air mixed with emanation was completely extracted by the pump, and collected in a tube over mercury.



To measure the amount of emanation, this air was introduced into a previously exhausted gold-leaf electroscope.*

The volume of the electroscope exceeded that of the air containing emanation. When the latter had been introduced, ordinary air was admitted to atmospheric pressure.

The electroscope was allowed to stand for three hours, in order to let the active deposit attain its equilibrium value. The rate of leak was then taken, the same 20 divisions of the microscope scale being always employed. A correction was applied for the rate of leak of the electroscope, when filled with air only.

I shall not give the detailed data for all the experiments, but only the final result. One case, however, may be given in detail, for the sake of example.

Æschynite, Ural Mountains—

Quantity taken 0.484 gramme.

Leak due to emanation collected in 24 hours—

20 div. in 3 m. 44 s., 3 m. 35 s., 3 m. 41 s.

Mean..... 3 m. 40 s.

Thus rate of leak = 327 div. per hour.

With air, the rate of leak was 7 div. per hour.

Subtracting this, corrected rate = 320 per hour or, per gramme of the mineral, 660 per hour.

A second determination, on about twice the quantity, gave 647 per hour.

On collecting a day's emanation a second time from the same portion of the mineral, the original value is recovered with a discrepancy of not more than 4 per cent.

The method described gives only a relative measure of the amount of radium present. To reduce it to absolute measure, the following method was employed.

Ten milligrammes of radium bromide, sold as pure, was employed as the ultimate standard of reference. This was placed near an electroscope, a plate of lead 1.5 cm. thick being interposed.

The rate of leak due to the radium was 924 scale divisions per hour, produced, of course, by the γ rays. The tube of pure radium bromide was now removed, and a tube containing 1.895 grammes of a much less concentrated preparation was substituted. This produced a rate of leak of

* In doing this, the methods of gas manipulation developed by Sir W. Ramsay and Dr. Travers were employed.

only 7.4 scale divisions per hour. Since the rays concerned in this experiment were able to penetrate a thick leaden block, we may neglect their absorption in the radio-active material itself, and in the glass tube containing it. Thus the rate of leak becomes a measure of the total amount of radium bromide present. The amount of radium bromide present in 1 gramme of the weaker preparation is accordingly $\frac{0.01 \times 7.4}{1.895 \times 924} = 4.24 \times 10^{-5}$ gramme.

Having determined the value of the weaker preparation in this way, 46 milligrammes of it were weighed out, and dissolved in water. The solution was made up to 100 c.c., and 5 c.c. (= 2.3 milligrammes) withdrawn with a pipette. This 5 c.c. of solution was placed in a flask, and the rate of leak, due to one day's accumulation of its emanation, was measured, as in the case of the decomposed minerals.

The corrected value was 644 scale divisions per hour. Thus 1 scale division per hour corresponds to $\frac{4.24 \times 10^{-5} \times 0.0023}{644} = 1.51 \times 10^{-10}$ gramme radium bromide.

It may, perhaps, seem at first sight to have been superfluous to use the weaker preparation, instead of working straight from the pure one, diluting it to the necessary extent.

The weighing out of pure radium salts is, however, an undesirable operation, even if a suitable balance for such work had been at hand, which it was not. For there is always the risk of loss of the valuable salt, with the attendant disadvantage of making the laboratory unfit for experiments in radio-activity. With the method adopted, it was not necessary to remove the salt from the hermetically sealed vessel which contained it.

The reduction of the radium determinations to absolute measure is subject to the assumption that the standard specimen of radium bromide contained 10 milligrammes of the pure material. This I cannot vouch for personally, but it is not likely to be far from the truth. The relative measurements of the quantity of radium are not subject to this source of uncertainty, and they alone are principally concerned in this investigation.

In stating the results, I shall express them as percentages of radium bromide in the mineral. This mode of expression is, of course, a fiction in one sense, as there is probably no bromine in the mineral. But the fiction is convenient, as the actual standard of comparison is bromide, and all that is meant is that the percentage of radium is what would be contained in that percentage of bromide.

Determination of Thorium.

The amount of thorium in a mineral can, of course, be determined by the orthodox methods of chemical analysis. The determination is not, however, an easy one, and cases are on record where even experienced analysts have been altogether mistaken as to the proportion present. For this reason, and also to economise time, I have determined thorium in the mineral by means of the thorium emanation. A weighed portion of the mineral was brought into solution. The solution was placed in a long glass tube slightly inclined to the horizontal. Air could be drawn by means of a filter pump through the tube, and carried the thorium emanation with it, into a well insulated testing vessel, connected with an electroscope.

The solution was, in each case, made up to a standard volume, and the air current was quite constant, since the pump was supplied from a shallow cistern overhead, giving a constant water pressure.

Thus the circumstances under which the bubbling took place were in each case the same. It was found that the rate of collapse of the electroscope* was proportional to the amount of thorium present in the solution.

The majority of the minerals contained radium as well as thorium. It is necessary to inquire, therefore, whether any part of the effect attributed to thorium emanation might have been really due to radium emanation. When the bubbling commenced, after the solution had stood for some time, there was a perceptible effect due to accumulated radium emanation, but this soon passed off. The readings for thorium were not taken until the bubbling had continued long enough to wash out all accumulated radium emanation, so that the rate of leak no longer diminished. One hour amply sufficed for this. The radium emanation was not generated fast enough to produce a measurable effect, after the accumulation had been got rid of. This was conclusively shown by the behaviour of minerals like Joachimsthal pitchblende, containing much radium and no thorium.

To reduce the thorium determinations to absolute measure, it is necessary to make use of a preparation of known thoria percentage. I did not find commercial thorium nitrate of sufficient purity for the purpose, and have therefore employed the thorium mineral from Ceylon, called thorianite. Concordant analyses of this, made at the Imperial Institute, and in Sir William Ramsay's laboratory, show that it contains about 77 per cent. of thoria. Different samples do not vary much amongst themselves.

0.153 gramme of this mineral gave a rate of leak of 360 scale divisions per

* Corrected, of course, for its natural rate of collapse.

hour. Corrected for the normal leak of the electroscope this becomes 346. Thus 1 scale division per hour represents $0.153 \times 0.77/346$, or 3.41×10^{-4} gramme of thorium oxide.

The following example may be quoted, to illustrate the determination of thoria by this method. 1.046 of grammes of samarskite from North Carolina was brought into solution. Air bubbled through it gave a rate of leak of 58.7, or corrected, 44.7.

Thus the rate of leak per gramme is $44.7/1.046$, or 42.7, and the thoria percentage is 42.7×0.341 , or 1.46.

Determination of Helium.

For this determination the method described by Dr. Travers* was employed. It consists in placing a weighed portion of the powdered mineral in a glass tube, with strong sulphuric acid, the powder being, however, initially supported out of reach of the latter. The tube is exhausted and sealed. It is then inverted and shaken, so that the acid is brought into contact with the powder. The tube is then heated in an air bath to 200° C., until the mineral is seen to be completely decomposed. This, in some cases, occurs very quickly. In others, it takes as long as a week. The gases are extracted by means of a mercury pump, the tip of the sealed tube being broken off inside an indiarubber connection.

The helium thus extracted is almost invariably mixed with other gases. To remove them it is necessary to mix with oxygen and spark the mixture over caustic soda. This was done in a gas burette with platinum wires sealed in. When, on prolonged sparking, no further contraction could be detected, the excess of oxygen was removed by bubbling the gas up into a tube with a little melted phosphorus floating on the top of the mercury.

The residue was measured as helium. In those cases where it amounted to $1/5$ of a c.c. or more, this was done in a gas-measuring tube of very small diameter, graduated in millimetres, and calibrated. Smaller quantities were measured in the capillary syphon of the gas burette. The cross section of this capillary was known, so that the length of the piston of gas (confined by mercury) determined the volume; in taking the measurement the levels were arranged so that the pressure was atmospheric.

It would, no doubt, have added to the completeness of the investigation if the gas had been spectroscopically examined in each case, to make sure that it did really consist of helium and nothing else. Some uncertainty attaches to those cases where the quantity of residual gas was less than $1/10$ of a c.c.

* 'The Study of Gases.'

per gramme, and I am not able to feel any confidence in the numbers given for quantities smaller than this, except as superior limits to the quantity of helium which can be present. It would not be difficult to make certain of quantities much smaller than this, by starting with a sufficiently large quantity of the mineral. But such determinations do not, as will be seen in the sequel, at present promise information of special value. The present experiments may be relied on as determining how much helium is present in the minerals in those cases where the quantity of gas exceeds 1/10 c.c. per gramme. In some experiments the helium was sparked again with oxygen and measured a second time. But no perceptible alteration of volume occurred. This proved the completeness of the purification.

Determination of Total Activity.

In addition to the determinations already mentioned, the activities of the powdered minerals were compared in the ordinary way, by means of the electroscope, with that of uranium oxide U_3O_8 . Such observations do not admit of any very simple interpretation, particularly not in the case of thorium minerals, where the leak observed depends much more on the emanating power than on the percentage of thorium present. Nevertheless it must not be forgotten that observations of this kind led to the discovery of radium, and it would be a mistake to despise them.

Sec. 3.—Experimental Results.

Having explained the methods adopted for determining the various constituents, the results may now be tabulated (see p. 95).

Sec. 4.—Connection between Uranium and Radium.

While this investigation was in progress, Mr. B. Boltwood published some measurements, from which he concluded that the amount of radium in a mineral was approximately proportional to the uranium.* The most interesting conclusion of the present investigation was in this way anticipated. Additional confirmation of a conclusion so important is not, however, superfluous, and the numbers given above amply afford it. The ratio of radium to uranium is given in the last column of the table, and varies very little for the different minerals. The only notable exception is in the pyromorphite previously examined by M. Danne. Mr. Fenton has very kindly confirmed the conclusion that this contains no trace of uranium. M. Danne

* 'Am. Jour. Science,' vol. 18, p. 97.

Mineral.	Locality where found.	Radium bromide, millionths of 1 per cent.	Uranium oxide (U ₂ O ₅), per cent.	Thorium oxide (ThO ₂), per cent.	Helium, cubic centimetres per gramme of mineral.	Total activity, uranium oxide (U ₂ O ₅), taken as unit.	Ratio of radium to uranium.
Pitchblende	J Joachimsthal	153.0	73.5	0	0.107	3.11	2.10
Cupro-uranite	Cornwall	120.0	60.0*	0	0.10	2.00	2.00
Pitchblende	Cornwall	60.6	29.15	0	0.08	0.867	2.00
Pitchblende	Near Grampound Road Station, Cornwall	48.5	21.23	0	0.10	1.17	2.28
Thorianite†	Ceylon.....	30.4	13.0	77	8.9	2.48	2.34
Æschynite	Hitterøe, Norway	24.0	9.43	1.26	1.09	0.606	2.54
Samarakite	N. Carolina, U.S.A.	22.5	10.30	1.46	1.5	0.495	2.18
Gradolite (?)‡	Ytterby	11.7	2.94	8.60	2.43	0.380	3.98
Æschynite	Ural Mountains	9.90	2.50	8.18	0.98	0.249	3.99
Cyrtolite	Llano Co., Texas	8.98	3.67	5.06	1.15	0.468	2.45
Silpilate	Little Friar Mountain, Virginia	8.82	2.86	4.92§	0.59	0.514	3.08
Kuxenite	Arendal, Norway	5.56	2.84	2.72	0.73	0.245	1.96
Carnotite 	Montrose Co., Colorado ..	5.27	2.98	0	0.01	0.174	1.76
Pyromorphite¶	Isny L'Évêque, France.....	4.39	0	0	0.02	0.0655	∞
Microtite	Amelia Court House, Vir- ginia	3.70	1.89	0	0.05	0.101	1.96
Orangite	Brevig, Norway	2.82	1.0**	48.5	0.11	1.07	2.82
Monasite I	Norway	2.35	1.0**	0.650	1.54	0.316	2.35
Monasite	Amelia Court House, Vir- ginia	0.806	0.1**	2.43	1.57	0.101	0.8
Kolm††	Sweden	0.670	0.377	0	—	0.0174	1.78
Monasite	Fahlun, Sweden.....	0.323	—	0.8	1.4	0.884	—
Monasite	Brazil	0.288	—	1.54	0.81	0.0654	—
Monasite II	Norway	0.275	—	1.21	2.41	0.373	—

* This number was assumed from various published analyses of the mineral, which are very concordant. The crystals are transparent, and it was possible to pick them out from the matrix in such a manner as to ensure purity.

† See 'Nature,' vol. 69, p. 510.

‡ I am not satisfied that this mineral is correctly named, for the amounts of uranium, thorium, and helium contained are all much larger than published analyses would indicate. Fortunately the name is of little importance for the present purpose.

§ The presence of thorium in this mineral seems to have escaped previous observers.

|| This mineral is finely disseminated throughout a sandstone matrix; it was not thought necessary to separate it, but a quantity was uniformly powdered with the matrix. This explains the low uranium percentage given, as compared with that of the pure mineral.

¶ This is the mineral recently described by M. J. Danne ('Comptes Rendus,' January 23, 1905), and I am indebted to his kindness for the sample.

** These determinations of uranium were rough ones only, very kindly made for me by my friend Mr. H. J. H. Fenton, F.R.S., on a small quantity of material.

†† This is a bituminous material, occurring in alum slate, in Sweden. Its radio-activity was detected by Mr. John Landin, of Stockholm, and he most kindly sent the sample. The material is said to be very abundant where it occurs. About two-thirds of it can be burnt away, leaving one-third by weight of ash. This ash contains the radio-active constituents. In making the determinations, a sample of the mineral was burnt, the ash being weighed. The percentages of radium and uranium in this ash were determined, and afterwards referred back to the weight of the unburnt mineral.

has given reasons for thinking that in this case the radium has been introduced from extraneous sources by infiltrating water. It may be that the slight discrepancies in the ratios found for the other minerals are referable to similar causes. As to the reality of these discrepancies I cannot vouch personally, not having made the uranium determinations myself.

The investigation has brought out the presence of uranium in several minerals—monazite and kolm, for instance, which were not previously known to contain it.* One of the monazites (from Virginia, U.S.A.) does not appear to contain as much uranium as it should. There should be 0.3 per cent. U_3O_8 ; whereas the actual quantity, as roughly estimated by Mr. Fenton, was 0.1 per cent. It is, however, difficult to even detect such a small quantity of uranium in presence of phosphoric acid, so not much stress can be laid on the discrepancy.

Sec. 5.—*The Presence of Thorium.* (Amended March 6.)

Thorium, it will be observed, seems to be invariably accompanied by the uranium-radium association. I have searched in vain for a thorium mineral free from radium, though many more than those mentioned above have been examined. Uranium-radium minerals free from thorium are easily to be met with. But never, so far as my experience goes, the converse. The ratio varies within wide limits; but still, the fact of the association of these rare substances seems to be suggestive.

Thorium is radio-active; it is, therefore, presumably changing into something. Professor Rutherford has estimated the time which half of a given quantity of thorium takes to disintegrate at 3×10^9 years.†

We may, without improbability, assume as a working hypothesis that these minerals are not less than 30 million years old. In that time, about $\frac{1}{2}$ per cent. of the thorium would have changed, so that the resulting product should have accumulated in weighable quantity. Helium, as we shall see, is probably a product. But it seems unlikely that the greater part of the *débris* takes this form, for the theory now most in favour (though very far from proved) is that the expelled α particles constitute the helium—that it is, in fact, a collateral product, not in the main line of descent.

What, then, is the most likely product? Uranium seems to fulfil some requirements, for it is, as we have seen, invariably present with thorium, and

* See, for instance, "Les Terres Rares," by P. Truchot, where many analyses of monazite are given, but none include uranium.

† 'Phil. Trans.,' A, vol. 204, p. 206.

is fairly rare, like its assumed parent. The existence of uranium minerals in which thorium does not occur, presents no difficulty. For the rate of disintegration of uranium is so small that, unlike radium, it may well be old enough to have originated in situations very different from those in which we find it. We cannot expect that the uranium should be proportional to the thorium, for the minerals are probably not old enough for radio-active equilibrium between these constituents.

The really serious objection to this view is that the atomic weight of thorium (232.5), is commonly taken to be greater than that of uranium (238.5). Professor McLeod has, however, drawn my attention to a paper by Baskerville,* in which he finds that thorium contains a constituent of higher atomic weight (256) than uranium (238.5). If this result should be confirmed by further investigation, the objection will be removed.

The view above explained is not one which I wish at all to press. It seems, however, to have sufficient experimental support to be worthy of mention. It is quite possible that one of the cerium metals, not uranium, is the next fairly permanent descendant of thorium; for these metals are almost, if not quite, always found with it. The question of this latter association deserves further experimental inquiry. I have not found the analyses quoted in mineralogical works of much use except to suggest which minerals would repay investigation. For, if not made with a view to the particular inquiry, the essential point is very liable to be missed. The existence of small quantities of cerium metals with thorium might easily be overlooked, for instance, if attention were not concentrated on the question of whether they were present.

Sec. 6.—*The Presence of Helium.*

Estimate of the Age of the Minerals.—The principal point in connection with helium brought out by these determinations is the way in which it is associated with thorium. In no case is any mineral found to contain more than a trace of helium, unless it contains thorium also. This is strong evidence that the greater part of the helium has been produced by thorium. To bring the point out more clearly, the minerals are re-arranged in the following table, in order of helium content:—

* 'J. Am. Chem. Soc.,' 1904, vol. 26, p. 922; see also "Report of International Committee on Atomic Weights," 'Proc. Chem. Soc.,' vol. 21, No. 288, January 18, 1905.

Mineral.	Locality.	Helium, cubic centi- metres per gramme.	Thorium oxide, per cent.	Radium bromide, millionths of 1 per cent.
Thorianite	Ceylon	8.9	77.0	30.4
Gadolinite ? ...	Ytterby	2.43	8.60	11.7
Monazite II ...	Norway	2.41	1.21	0.275
Monazite	Virginia	1.57	2.43	0.806
Monazite I.....	Norway	1.54	0.650	2.35
Samarskite ...	N. Carolina	1.50	1.46	22.5
Monazite	Fahlun	1.40	0.80	0.323
Cyrtolite	Llano Co., Texas	1.15	5.05	8.98
Æschynite.....	Hitteroe, Norway.....	1.09	1.26	24.0
Æschynite.....	Ural Mountains	0.98	8.18	9.90
Monazite	Brazil.....	0.81	1.54	0.288
Euxenite	Arendal, Norway	0.73	1.96	5.56
Sipilite	Little Friar Mountain	0.59	4.92	8.82
Orangite	Brevig	0.11	48.5	2.82
Pitchblende ...	Joachimsthal.....	0.107	0	153.0
Pitchblende ...	Grampound Road, Corn- wall	0.10	0	48.5
Cupro-uranite...	Cornwall	0.10	0	120.0
Pitchblende ...	Cornwall	0.08	0	60.6
Microlite	Virginia.....	0.05	0	3.70
Pyromorphite	Issy L'Evêque	0.02	0	4.39
Carnotite	Montrose Co., Colorado ...	0.01	0	5.27

It will be noted that although when much helium is found, thorium is found also, the converse does not hold. For orangite, the second richest thorium mineral, contains very little helium. This, however, does not appreciably weaken the evidence in favour of the view that thorium produced helium, for the conditions in this mineral may not have been favourable to the retention of helium when formed. Even apart from this consideration, no definite quantitative relation between helium and thorium or between helium and radium can be expected, for the helium, which is an inactive product, will accumulate indefinitely, and will not come to radioactive equilibrium, decaying as fast as it is generated. Everything, therefore, depends on how long the process has been at work. It is curious to note how little helium even the richest radium-uranium minerals seem to contain, when they do not contain thorium too. This suggests that, since the production of helium from radium has been observed experimentally, the same experiment might be practicable with a manageable quantity of thorium. I have

searched in vain for a thorium mineral quite free from radium; some of the monazites, however, in the above list, contain only very little radium, but much helium. In fact, the monazite of lowest radium content has, as it happens, the most helium of all. This all goes to strengthen the conclusion that thorium produces helium. I have examined the list of helium bearing minerals given by Sir William Ramsay.* In no case has helium been found in a mineral not known to be radio-active.

If we could assume that helium was produced by radium only, and that amount of radium remained constant, then the amount of helium in a mineral would obviously give an inferior limit to its age—only a limit, because the helium may not have been all retained. Take, for instance, the mineral thorianite; Ramsay and Soddy† have estimated that 1 gramme of radium bromide gives 0.0022 milligramme of helium in a year. One gramme of the mineral gives 8.9 c.c. of helium, and contains 3.04×10^{-7} gramme of radium bromide. This quantity of radium produces in a year 6.70×10^{-13} gramme = 3.71×10^{-9} c.c. of helium. The time required to produce the observed amount of helium would be, therefore,

$$\frac{8.9}{3.71 \times 10^{-9}} = 2.40 \times 10^9 \text{ years, about 2,000,000,000 years.}$$

Professor Rutherford‡ has estimated the time of decay of uranium to half its initial value to be of this order (10^9 years), so that there is reason for thinking that the amount of radium, which at any time is proportional to the uranium, can have been in the mean very materially more than what it is now, during the last 2,000,000,000 years.

The real weakness of the argument lies in the uncertainty as to whether thorium does not produce helium. As we have seen, the probabilities seem to be strong that it does. This objection does not apply to the minerals free from thorium; one of the Cornish pitchblendes, for instance, contains 4.85×10^{-7} gramme of radium bromide and 0.1 c.c. of helium per gramme. The age in this case cannot be less than 1.68×10^7 , or about 20,000,000 years. In no case of this kind is a much larger age limit indicated.

Sec. 7.—*Thorium Emanating Power of Minerals.*

I have given above the determinations of thorium made by bubbling air through a solution of the mineral. It was interesting to determine how far the powdered mineral would serve the purpose, whether, in fact, the minerals were in an emanating condition or not.

* 'Annales de Chimie,' 7th Series, vol. 13, p. 440.

† 'Roy. Soc. Proc.,' vol. 70, p. 353.

‡ 'Phil. Trans.,' A, vol. 204, p. 206.

A piece of glass tube, about 10 cm. long and 0·5 cm. internal diameter was loosely packed with the powdered mineral confined between plugs of cotton wool, and air was drawn over it at a constant rate through a testing vessel as when the solution was used. The comparative rates of leak were as in the following table. The thoria percentages are given for comparison :—

Mineral.	Locality.	Thorium oxide, per cent.	Thorium emanating power, arbitrary scale.
Thorianite	Ceylon	77·0	588·0
Orangite	Brevig	48·5	242·0
Gadolinite	Ytterby	8·60	50·0
Æschynite.....	Ural Mountains.....	8·18	40·0
Cyrtolite	Llano Co., Texas	5·05	1248·0
Sipilite	Little Friar Mountain ...	4·92	140·0
Monazite	Virginia	2·43	144·0
Euxenite	Arendal, Norway	1·96	208·0
Monazite	Brazil	1·54	2·7
Samarskite.....	N. Carolina	1·46	5·0
Æschynite.....	Hitteroe.....	1·26	3·0
Monazite II	Norway	1·21	610·0
Monazite	Fahlun	0·80	688·0
Monazite I.....	Norway	0·650	217·0

It will be seen that there are very great variations between the emanating power of the solid and the emanating power of the solution. In some cases a much greater fraction of the emanation generated by the solid can escape, than in others. Some of the minerals are, in fact, in a de-emanated condition, others are not. The emanating power of the solid cannot be trusted even as a rough quantitative test of the amount of thorium present. None the less, it forms a very valuable indication of the presence of this element, though of no use to prove its absence. Granted the apparatus ready for use, it is possible in many cases to prove the presence of thorium in as many minutes as the chemical tests would require days.

Sec. 8.—*Conclusion.*

There are two outstanding radio-active substances which are not included in the present investigation, actinium and polonium. With regard to actinium, I have not attempted anything. There is no practical way of

determining this constituent at present; the actinium emanation would give the best chance, but actinium is so scarce that in most cases there would probably be sufficient traces of thorium to mask its presence. The chemical separation of these elements is unfortunately by no means easy.

I have made a good many experiments on polonium; this part of the investigation is incomplete, but it does not seem desirable to defer publication longer, so that the conclusions must be reserved for a future communication.

I have not yet succeeded in working out a satisfactory method of measuring the amount of polonium in a mineral. Experiments are, however, in progress to determine the rate of decay of the active matter which deposits from solutions of the several minerals on to a bismuth plate. It will be necessary to wait a little longer for conclusive results, but the measurements hitherto made are not at all favourable to the identity of the bismuth-plate deposits from the several minerals.

The results of this paper may be summarised as follows:—

(1) The conclusion that the amount of radium in a mineral is proportional to the uranium, is confirmed. The investigation of this point has brought to light the existence of uranium in some minerals not previously known to contain it, monazite, for instance.

(2) It is shown that thorium minerals invariably contain the uranium-radium combination. This observation is difficult to interpret, but it may possibly indicate that thorium is producing uranium.

(3) Helium never occurs except in very minute quantity unless thorium is present. The helium of minerals, therefore, is probably produced more by thorium than by radium.

(4) Thorium minerals vary much in emanating power. Some retain nearly all their emanation, others give off large quantities.

In conclusion, I must express my thanks to several kind friends and correspondents, who have given me samples of minerals, including Professor J. W. Mallet, Sir W. Ramsay, the late Mr. W. Shapleigh, and Mr. John Landin. Mr. H. J. H. Fenton has most kindly helped by testing some of the minerals for uranium.

*The Rate of Transmission of the Guatemala Earthquake,
April 19, 1902.*

By R. D. OLDHAM.

(Communicated by Professor John Milne, F.R.S. Received February 10,—Read
March 9, 1905.)

In 1900 I showed,* by a critical examination of the records of earthquakes, obtained at a distance from their origin, that three distinct forms of wave motion could be recognized, to which I applied the terms first, second and third phase, and that these travelled along different paths and at different speeds. It was suggested that the first and second phases represented the outcrop of condensational and distortional mass waves, which had travelled through the earth, and that the third phase was due to waves, partly elastic and partly gravitational, which had travelled along or near the surface. These explanations have not been universally accepted, and alternative suggestions have been made, but the distinction of the three phases has been generally recognized, the nomenclature adopted, and the first two phases accepted as mass waves travelling through the earth. This last conclusion has been borne out by the time-curves published by Professor Milne, who, using data whose greater abundance compensated for a lesser degree of precision, deduced a set of time-curves essentially identical with mine, in that they showed a curvature in the first two phases which is only compatible with the supposition that they belong to mass waves.†

In Japan these conclusions have never been formally traversed, but in the more recent publications of that country we find that no less than eight phases are recognized, and designated by the symbols $P_1, P_2 \dots P_8$; of these P_1 and P_2 correspond to the first and second phases of the last paragraph, while the remainder constitute the third phase. The nature of these third phase waves is still a very open question, and it is doubtful whether there is any real difference in the character of the wave motion of P_3, P_4, P_5 , etc., or whether we are not dealing with waves of essentially similar nature, whose rate of propagation is a function of their period; in any case it is acknowledged that these waves are propagated along or close below the surface of the earth. The same conclusion is, however, also adopted for the first two phases, and the

* 'Phil. Trans.,' A, vol. 194, pp. 135—174 (1900).

† 'British Assoc. Rep.,' 1902, p. 66.

rectilinear character of their time curves apparently established by Dr. Imamura, on the basis of a large number of observations.*

As this point is of some importance, it seems desirable to devote a few words to the consideration of the nature of the evidence on which the curves are drawn. I find that of 85 earthquakes dealt with, 31 originated in or near Japan, and no record except that at Tokio is given; of the remaining 54, the time and place of origin was known by direct observation in only five cases, in one of which the time adopted is erroneous; in three more the place but not the time of origin was known, in 25 the place of origin is only approximately known, and in 21 it is inferred from observations at a distance. In all these 49 earthquakes the time of origin was calculated from observations at a distance, by the use of a formula based on the assumption of a uniform apparent rate of propagation; in these circumstances it is not surprising that the resulting intervals show a close approximation to a rectilinear time-curve.

Of the five earthquakes whose time and place of origin were supposed to be known with accuracy, great importance is attached to that of April 19, 1902, originating in Guatemala, and Dr. Imamura has made a detailed study† of it which he regards as supporting his views, but he was misled as to the time of origin, and, moreover, obtained his times, other than those of commencements, from figures published in the *British Association Earthquake Circular*, No. 6. As these figures are printed from blocks, which were drawn from photographic copies of the original traces, the times obtained from them naturally differ from those obtained by direct measurement on the original trace, or on a photographic copy of it.

In these circumstances it has seemed desirable to re-examine the records of this earthquake, and to determine, so far as possible, the true time of arrival of, at least, the first and second phases of wave motion at all stations where they were recorded. By the generosity of Professor Milne, who placed at my disposal not only the photographic copies of the records of the Milne pendulum stations, but also the reports from other observatories and the correspondence relating to the time of origin, it has been possible to compile a record of this earthquake more complete than has yet been published in the case of any other.

Sec. 2. *Definitions.*—Before proceeding to the consideration of the records it is desirable to define the exact sense in which the words first, second, and third phase are used and interpreted from the records.

* 'Publications, Earthq. Investigation Comm. Foreign Languages,' No. 16 (1904).

† 'Publications, Earthq. Investigation Comm.,' No. 16, p. 112

The *first phase* is normally the commencement of the record: as exceptions we may find that—

(1) The instrument is affected by tremors before the normal commencement, whether these belong to the same disturbance or an independent one.

(2) The instrument, failing to respond to the first impulse of the shock, may respond to a later impulse in those cases where the disturbance is caused by more than one original impulse.

(3) The instrument may fail to respond till the arrival of the wave motion due to the second or third phases.

Each of these causes of error is easily detected when a number of records are compared with each other.

The disturbance due to the first phase is seldom of more than small amplitude in the case of instruments recording the horizontal components of the motion; in the vertical component of the Vicentini instrument the disturbance due to this phase is greater than that of either of the other two.

The *second phase* is marked by an abrupt and considerable increase in the amplitude of the disturbance. In the case of pendula of five seconds or less in period the maximum amplitude is almost invariably found in this phase; the vertical component, on the other hand, rarely shows even the slightest disturbance. This distinction in the character of the records would, in itself, be sufficient to show that the first and second phase waves were very different in character. On instruments giving an open diagram, the period of the waves in this phase is always longer than in the first phase.

The *third phase* sets in with long period waves, followed by quicker, but always longer period than met with in the first two phases. In larger disturbances, at least, this phase is always accompanied by a certain amount of surface tilting, though this is apparently much less than was supposed a few years ago. In Europe it is usual to give the time of maximum amplitude of disturbance, and the practice seems useful, although the importance attached to these maxima has been questioned, and they have been regarded as diagrammatic, for which I should prefer to write *instrumental*.* The researches of Prince Galitzin† and Professor Rudzki‡ have shown that a perfectly frictionless horizontal pendulum would not record truly a regular periodic movement of its support, as it would acquire a pendular swing of its own, and the record would be a combination of this with that due to the movement of the ground. Seeing that the desire of constructors of seismographs has always

* A. Imamura, 'Rep. Tokyo Physico-Mathematical Society,' No. 20, p. 1 (1904).

† 'Comptes Rendus de la Comm. Sismique Permanente, St. Petersburg,' vol. 1, pp. 101—183 (1902).

‡ 'Beiträge z. Geophysik,' vol. 6, pp. 138—155 (1904).

been the most complete elimination of friction that they can attain, it is not improbable that these conclusions apply in a modified manner to the records of seismographs; in addition it must be remembered that there is probably no defined maximum of the disturbance recorded, and in view of these two considerations it is possible that too much importance has sometimes been attached to the exact time of maximum amplitude of the record. On the other hand, it is impossible to see the well-defined maxima, having often three or four times the amplitude of any other part of the record, which are not infrequent, without regarding them as recording a reality rather than a mere instrumental accident. For this reason I have followed custom in recording the time of maximum displacement in the third phase.

Sec. 3. *Place and time of origin.*—The place of origin can be determined with sufficient accuracy from the maps published by Messrs. Rockstroh* and G. Eisen.† From the former an origin may be deduced as in about N. lat. 15°, W. long. 92°; according to the latter in N. lat. 14°, W. long. 91° 30'. For the purpose of calculation of distances, the origin has been assumed as N. lat. 14° 30', W. long. 91° 15'.

The time was given by Mr. Rockstroh, on the strength of a single observation, as 8.25 P.M. local time; this was the time used by Dr. Imamura, but fortunately it can be checked, for it so happened that a block of buildings was set on fire by the overturning of a lamp, and burnt down at this time. The buildings were insured against fire, but not, as stipulated in the policy, against fire caused by earthquake, and it became a matter of importance to decide whether the lamp was upset by the earthquake, as claimed by the insurance company, or before the earthquake, as claimed by the owners; as a consequence of this dispute, the time of occurrence of the earthquake became the subject of careful inquiry, and the time finally accepted was 8.20 P.M. local time. The time used throughout the Republic of Guatemala is 6 h. 2 m. 3 s. slow of Greenwich mean time,‡ so the time of origin of the earthquake may be taken as 2 h. 22 m. Greenwich mean time.

Sec. 4. *The observations.*—As there does not seem to be any necessity for reprinting every published record of the earthquake, I shall merely give a

* 'Nature,' June 12, 1902.

† 'Bull. Amer. Geog. Soc.,' vol. 35, p. 325 (1903).

‡ J. Milne, "Civil Time," 'Geogr. Journ.,' February, 1899. For the particulars in this paragraph I am indebted to Professor Milne. The case may be quoted as a practical application of the new seismology; for the insurance company, when involved in the dispute, wrote to Shide, inquiring whether any information as to the true time of occurrence of the earthquake could be given, and the time deduced from the records of the British Association organisation proved to be within some seconds of the time finally adopted after local inquiry.

tabular statement of times and a note in explanation of the sources of information, and of any differences which may be found between the times given and those originally published.

Tabular Statement of the Recorded Time of Arrival of each of the Three Principal Phases of Wave Motion. Guatemala Earthquake of April 19, 1902. Times in Minutes after 2 hours Greenwich Mean Time.

Distance.	Station.	I phase.	II phase.	III phase.
		min.	min.	min.
27·8 }	Baltimore	30·1 }	35·6 }	40·3 }
30·8 }	Toronto	30·5 }	35·5 }	38·0 }
43·0	Victoria, B.C.	31·3	37·2	50·7
52·7	Cordoba, Arg.	32·1	39·1	45·3
76·2	Paisley	(22·0)	(43·0)	73·0
77·0 }	Edinburgh	36·0 }	45·5 }	74·5 }
77·4	Bidston	35·0	—	75·1
77·6	San Fernando	34·8	(43·3)	61·8
78·8 }	Shide	35·4 }	46·8 }	79·2 }
78·8	"	35·5	46·9	78·7
78·8	"	35·5	46·9	73·0
79·3 }	Kew	36·2 }	45·8 }	70·1 }
82·3	Uccle	36·0	46·4	—
84·9	Hamburg	36·3	46·6	80·4
85·0	Strassburg	36·2	—	—
88·6 }	Padua	36·6 }	47·0 }	69·6 }
88·6	"	36·6	(47·1)	69·7
88·6	"	{ 36·6	47·3	69·7
88·6	"	{ 36·6	47·3	73·4
88·7	Florence	37·0	47·4	68·0
88·7	"	36·7	47·2	70·0
88·7	"	36·0	46·1	68·0
90·2	Trieste	36·8	(48·9)	—
90·2	Rome	37·6	(50·3)	73·0
90·2	"	37·6	—	—
90·4	Quarto Castello	37·0	47·5	68·5
90·4	"	36·6	47·0	69·0
90·4 }	Rocca di Papa	{ 36·7 }	47·0 }	72·5 }
90·4	"	{ 36·8	48·3	—
90·4	"	36·7	47·1	76·8
90·4	"	36·8	47·1	71·2
90·4	"	{ 37·6	47·0	72·5
90·4	"	{ 37·6	47·0	—
91·4	Juriew	36·6	46·2	—
91·4	"	36·6	—	73·0
91·4	"	37·3	47·4	—
91·7	Ischia	37·0	47·6	72·0
92·4	Pawlovsk	—	47·2	73·3
93·6	Catania	{ 36·7	—	71·5
93·6 }	"	{ (41·0) }	— }	74·5 }

Tabular Statement—*continued*.

Distance.	Station.	I phase.	II phase.	III phase.
		min.	min.	min.
100·3 } 102·5 } 104·5 }	Nicolaiew Wellington, N.Z. Christchurch, N.Z.	37·0 } 38·0 } 37·2 }	(52·0 } 47·0 } 48·0 }	70·0 } 79·0 } 79·2 }
110·4 110·4 110·7 }	Tokio " Tiflis	(41·6) (38·8) 38·2 }	(49·6) (53·0) (56·6)	— — 86·1 }
110·7 110·7 110·7 }	" " "	38·2 } 38·2 } 38·3 }	(56·5) (56·4) (58·5)	86·0 } 85·2 } 85·9 }
111·9 } 111·9 } 111·9 }	Irkutsk " "	(43·7) (41·7) (43·2)	51·5 } (58·8) (58·5)	96·4 } 99·9 } 86·0 }
113·9 121·3 121·3	Capetown Tashkent..... "	38·4 } 39·9 40·5	51·6 } 49·2 50·1	— — —
142·9 144·1 144·1 }	Calcutta Bombay "	44·0 } 43·3 } 43·8 }	— } 64·5 } 66·8 }	(73·5) } 107·0 } 108·4 }
144·1 } 149·8 152·9 160·4	" Perth, W.A. Kodaikanal Batavia	43·4 } 43·8 } (39·0) 43·7	— } 62·0 } (59·4) 68·0	109·1 } — } 107·2 } 109·0 }

Note Explanatory of the Statement.—Each line refers to the record of a distinct instrument, or at least to an independent pendulum, except in the case where two consecutive records at the same station are bracketed together; in these cases the times refer to the two components into which the movement of a single mass is resolved. Figures enclosed in brackets indicate either that there is an uncertainty in the interpretation, or that a comparison of the times with those at other stations shows that they cannot refer to the phase of the record to which at first sight they would naturally be referred.

It will be observed that the list of records contains several groups of about equal distance from the origin, which are indicated by the long brackets on the right-hand side of each row of figures, and in dealing with the results it will be best to take the mean of each group, thereby eliminating, to a large extent, the minor errors which may affect individual observations. Treated in this way, we get the following series of group-averages of time of arrival, to which I have added the corresponding mean rate of transmission from the origin, expressed in degrees of arc per minute of time. This way of

expressing the rate of transmission seems preferable to the more usual one of kilometres per second, as the latter always requires qualification, being meaningless unless accompanied by a statement of the line along which the distance is measured.

Group-average Times of Commencement of First and Second Phases, and of Maximum of Third Phase; also Mean Apparent Rate of Propagation in Degrees per Minute.

Distance.	First phase.			Second phase.			Third phase, max.		
	Obs.	Time.	Rate.	Obs.	Time.	Rate.	Obs.	Time.	Rate.
deg.	No.	min.	deg. + min.	No.	min.	deg. + min.	No.	min.	deg. + min.
0° 0'	—	23·0	—	—	23·0	—	—	23·0	—
39° 3'	2	30·3	3·53	2	35·5	2·17	2	39·1	1·71
78° 0'	7	35·5	5·78	5	46·4	3·20	6	75·1	1·47
90° 8'	20	36·8	6·14	14	47·1	3·62	19	71·4	1·84
102° 4'	3	37·4	6·65	2	47·5	4·02	2	79·1	1·79
112° 2'	4	38·3	6·88	2	51·5	3·80	7	89·4	1·66
145° 6'	5	43·7	6·71	2	63·3	3·53	3	108·2	1·69
160° 4'	1	43·7	7·39	1	68·0	3·55	1	109·0	1·84

This statement shows that in the *first phase* the apparent rate of transmission increases continuously with the distance, if we except the decrease at about 145°, which may be due to the commencements being late, or to those in the group before it being early. In any case the figures show that the time-curve is not rectilinear, though the recorded times show an approximation to a uniform rate of about 9·7 degrees per minute between the limits of 30° and 90° from the origin. This part of the time-curves, as drawn by Professor Milne and by myself, shows an approximation to a straight line and the curvature only becomes conspicuous when they are extended beyond these limits. In the case of the Guatemala earthquakes, we have no observations at less than 28° from the origin, but the more distant records—if we except the aberrant one from Kodaikanal—seem to show that the emergence of this phase of wave motion was practically simultaneous from 140° to 160°, a phenomenon which might be explained on the hypothesis of mass waves, but not on that of waves propagated parallel to the surface. It is not, however, advisable to attach much importance to the more distant records till they have been confirmed by others; up to 90° from the origin we have a sufficiently complete series of mutually corroborative records.

The *second phase* shows the same feature as the first, of an increase of apparent rate of propagation with distance, but this only continues to about

100° from the origin; beyond that there seems to be a decrease. This result is unexpected, but must not be rejected merely on that account, yet it is worth noting that the second phase is much less well marked in these distant records than in the nearer ones. On the Milne pendula the absolute maximum of displacement is ascribed to this phase, but on the horizontal pendula with mechanical registration at Bombay, this phase is hardly marked on one and not at all on the other.

Of the *third phase* little need be said; the apparent rate of propagation is, on the whole, uniform, the irregularities being sufficiently accounted for by the causes referred to in Sec. 2.

The sources from which the data were taken are: for the Milne pendulum stations, the circulars of the Seismological Committee of the British Association; for the Italian records the 'Bolletino della Società Sismologica Italiana'; for the Russian records the 'Bulletin de la Commission Centrale Sismique Permanente'; and for other places the periodical reports of the observatories. In addition to these the examination of the photographic reproductions of the Milne pendulum records has enabled me to add particulars regarding the time of the second phase which are not given in the British Association circulars. A few Italian stations where only the time of commencement was recorded have been omitted. The notes following refer only to those cases where there has been any difficulty of interpretation, where this has been simple and straightforward it is not necessary to reprint the original record.

Paisley. The whole record is marked by air tremors, and only the time of maximum is determinable. The second phase seems to have commenced at 2 h. 43 m. or thereabouts.

San Fernando.—The second phase cannot be clearly distinguished from the effects of the successive impulses, recognizable on this as on other traces.

Tokyo.—From this place we have two records. One, by Professor Omori, in the British Association circular, which gives the commencement at 2 h. 41.6 m., L.W. commence at 2 h. 49.6 m., maximum 2 h. 50.9 m. The other, published by Dr. Imamura in his account of the Milne pendulum seismograms, obtained at Hongo, Tokyo,* gives the times as P_1 , 2 h. 38.8 m., P_2 , 2 h. 53.0 m., with an instrumental maximum shortly after. The reproduction of the seismogram does not help matters, as it differs so much in type from those at other stations: the time, 2 h. 38.8 m., is about what would be expected for the commencement from a comparison with other records, and 2 h. 49.6 m

* 'Publications, Earthq. Investigation Comm.,' No. 16, 1904, p. 89.

would not be far from the time for the second phase, but in view of the doubt attaching to the interpretation of the records from this station, I have thought it best to exclude them all.

Irkutsk.—All the instruments at this station appear to have commenced with the second impulse, which can be found on most records at about 4 m. after the first. On the Milne pendulum the recorded commencement is preceded by a small disturbance of the trace, whose beginning is gradual and cannot be fixed, though it is visible for some minutes. The second phase commencement is at 2 h. 51.5 m. on the Milne pendulum trace, the other times on this column are those recorded for reinforcements on the traces of two horizontal pendula.

Tashkent.—The first tremors are recorded at 2 h. 34.5 m. and 2 h. 34.8 m., the times in the table are those of the first reinforcements, which evidently correspond to the first phase in the records of other stations.

Bombay.—The recorded maximum is at 3 h. 8 m. or 3.5 m. after the first marked increase in amplitude, which is taken to represent the second phase. Slow oscillations, marking the third phase, set in at 3 h. 27 m., and are slowest at 3 h. 39 m., when the trace is quite open; they become quicker and attain a maximum amplitude, almost as great as that of 3 h. 8 m., at 3 h. 47 m.

Besides the Milne pendulum there are two heavy horizontal pendula. I am indebted to Dr. N. A. F. Moos for the tracings of their records, from which the following particulars have been taken.

Hor. Pend., E.W.—Commencement 2 h. 43.8 m.; at 3 h. 6.8 m. there is a sudden displacement and another, larger, at 3 h. 11.7 m., these consist in each case of a single oscillation and seem to represent the second phase, maximum of third phase at 3 h. 48.4 m.

Hor. Pend., N.S.—Commencement 2 h. 43.4 m.; the second phase is not recognisable; maximum of third phase at 3 h. 49.1 m.

Kodaikanal.—The record as given in the British Association Circular No. 6 is: commencement 2 h. 39.0 m., maxima 3 h. 0.4 m., 3 h. 6.7 m., 3 h. 10.8 m., 3 h. 47.2 m., 3 h. 52.3 m.; amplitudes, 0.8 mm., 0.5 mm., 0.5 mm., 0.4 mm., 0.5 mm. The trace itself shows a very small amplitude throughout, and the five maxima form a series of small bulges arranged in two groups of three each, the sixth being at 3 h. 56.5 m. Here the maximum at 3 h. 0.4 m. seems to belong to the second phase, which would then begin about 1 m. earlier.

The most remarkable feature about this record is the time; both commencement and second phase are some four or five minutes earlier than would be expected from the records at other observatories of about the same epicentral

distance. The easiest explanation would be to assume an error in the time, but this supposition is inadmissible in an astronomical observatory, one of whose functions is the giving of a daily time signal. The discrepancy must remain inexplicable, and in view of it, and of the doubt in the interpretation, the record has been excluded from consideration.

Batavia.—The diagram is rather indefinite; there is an increase at about 4 m. after the commencement, probably marking the second impulse, but the first considerable increase is about 25 minutes after the commencement. This probably represents the second phase, of which the beginning is indistinct, and to which the maximum at 3 h. 12.4 m. belongs; the maximum of the third phase is at about 3 h. 49 m.

*A Determination of the Amounts of Neon and Helium in
Atmospheric Air.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

(Received March 11,—Read March 16, 1905.)

Some time ago I communicated to the Society* the results of an attempt to estimate the amounts of krypton and of xenon in air. The quantities were necessarily minimum estimates, for there is no doubt that both krypton and xenon must evaporate when air evaporates, even if that take place at a very low temperature. Dr. Travers and I guessed at the amounts of neon and helium, and supposed that the amount of helium was one or two parts per million, and that of neon one or two parts per 100,000. This guess is not very far from the truth, as the following account of recent experiments will show.

The ingenious method discovered by Sir James Dewar of using cooled cocoanut charcoal as an absorbent for gases has made it easy to carry out the estimation. The process consists in cooling 100 grammes of such charcoal to -100° , approximately, in a bulb from which all air has been removed by a pump. Such charcoal will absorb about three litres of air; at that temperature neither neon nor helium are absorbed in appreciable quantity, as special experiments showed. Hence on placing the cooled bulb containing the charcoal in communication with a Töpler pump, the uncondensed gases enter the barrel of the pump. On closing the connecting stop-cock, a further quantity

* 'Roy. Soc. Proc.,' vol. 71, p. 421.

of gas accumulates, and is again removed into the pump in the same manner. As the relative volumes of the pump and of the cooled bulb were approximately 4 to 1, after communication had been established four times, only $1/256$ of the contents of the bulb were left in it. And as the gas in contact with charcoal exerts a kind of vapour-pressure, inasmuch as the pressure which it gives depends on the temperature as well as on the extent of the surface of charcoal to which it is exposed, it may be assumed that gas escapes from the charcoal on each reduction of pressure, and that the more volatile gases in the bulb should be expelled by the less volatile.

In this manner 18 litres of moist air was treated; on its way to the charcoal bulb it traversed a tube filled with phosphorus pentoxide, to deprive it of moisture. The temperature was about 15° during these operations, hence the actual volume corrected to 0° C., and deprived of water-vapour, was about 16,800 c.c. This volume was reduced to about 400 c.c. in the manner described, and the smaller volume contained practically all the neon and helium.

By means of a smaller apparatus containing about 3 grammes of charcoal, the volume was further reduced, in a similar manner, until only a few cubic centimetres were removed through the pump. A convenient cooling mixture was found to be frozen ether. By stirring ordinary commercial ether with a test-tube containing liquid air, and frequently replenished, solid ether at last begins to coat the outside of the test-tube. At this stage liquid air is poured on to the surface of the ether, and a crust of ether-ice forms. This is broken, and stirred through the liquid portion, and the operation is repeated until a sufficient quantity of solid has accumulated. The cold ether bath may now be used to cool the charcoal tube; not much solid melts during the process, and the temperature registered by a pentane thermometer was approximately -100° .

Having reduced the volume of the gases to about 2 c.c., the remaining oxygen and nitrogen were removed by sparking. It is true that about $2/100$ of a cubic centimetre of argon may be thus retained; but the quantity is probably much less, for oxygen is less volatile than argon, and would probably remove at least a portion. The residue, at any rate, did not show the argon spectrum.

The inert residue was then, after it had been measured, admitted into the small apparatus; the charcoal, however, was now cooled with liquid air. Preliminary experiments had shown that at that temperature, neon is retained by charcoal in considerable amount. Hence, on opening the stop-cock communicating with the pump, helium escaped, while neon was retained

The surface of the charcoal was very large considering the small quantity of gas presented to it. As before, the pump was opened four times, so as to make sure that all helium should escape. This helium showed the neon spectrum, but feebly; it may have contained a few per cent. of neon. On the other hand, the neon remaining in the charcoal, when expelled by heat, was almost free from the helium spectrum. Probably then, the estimate which will be given errs in that the quantity of helium may be somewhat too large, and that of neon too small. The neon was again purified by sparking before being measured; for it was thought best to jacket the charcoal tube with the vapour of boiling quinoline (237°) in order to make sure that all neon had been expelled, and the effect was to expel along with it some nitrogen which had remained in the charcoal, besides some carbon dioxide.

A word may be said as to the method of measuring very small quantities of gas. The measuring tube was provided with a 2-way stop-cock, one exit from which was sealed to an inverted siphon of capillary tubing. It had also two points of blue glass sealed in, one indicating the volume 2.409 c.c., the other 9.657 c.c. The smaller volume was alone used. In reading the volume of the gas, the measuring tube is clamped in front of a long standard scale (one by Zeiss, which had been calibrated). The mercury is then set to the blue glass point, by lowering the mercury reservoir attached to the measuring tube, and the temperature, and difference in level of the two mercury surfaces, are read. The volume at 0° and 760 mm. pressure was calculated in the usual way.

The excellent results given by this method will be seen from the correspondence between the volume of mixed neon and helium, and the sum of the measurements of each separately.

Volumes of Neon and Helium.

Volume of mixed gases, after sparking	0.2756 c.c.
„ helium, unsparked	0.0685 „
„ neon, after sparking.....	0.2080 „

The sum of the last two is 0.2765, a number agreeing within $\frac{1}{2}$ per cent. of the volume taken.

Referring these quantities to the volume of air from which they were extracted, and also to that of the argon in that air, we obtain:—

Neon in air.....	1	volume in 80,790 volumes of air.
Helium in air.....	1	„ 245,300 „ „
Together	1	„ 61,000 „ „

The percentage of argon in air being taken as 0·937, there follows:—

Neon in argon.....	1	volume in 757	volumes of argon.		
Helium in argon	1	„	2300	„	„
Together	1	„	571	„	„

The percentages by weight and volume are as follows:—

Neon by weight in gaseous air...	0·0000086	per cent.
„ volume „	„	0·0000123 „
Helium by weight „	„	0·00000056 „
„ volume „	„	0·00000040 „

The density of crude argon was determined by Lord Rayleigh and myself as 19·94; the mean density of pure argon, in conjunction with Dr. Travers, as 19·957. It is interesting to see whether, neglecting the heavier constituents (inasmuch as their amount is inappreciable), the calculated and found densities of argon agree. Allowing for the presence of the neon and helium, the density of pure argon should be 19·953; the most reliable numbers found by Travers and myself were 19·952 and 19·961.

One more point deserves notice. A fair quantity of the mixture of neon and helium was prepared by liquefying air; 540 c.c. of liquid air were collected. The lighter gases were collected by blowing air through this liquid, and collecting in a gas-holder. This mixture was then fractionated by absorption in charcoal, as already described, but the charcoal was cooled with liquid air to -192° ; the mixed gases measured 4·463 c.c. Now, taking the density of liquid air as 1, the total volume of the gaseous air from which the 540 c.c. of liquid air had been obtained was 404·4 litres at 0° and 760 mm.; and the proportion of mixed gases in gaseous air would be 1 in 90,000. A considerable quantity of neon, and possibly a trace of helium, had apparently been retained by the charcoal. But the yield on a large scale is not a bad one; and no doubt, if the charcoal were cooled not below -100° , all the gases could be extracted.

Now this gas must have contained all the free hydrogen present in the air; and it was mixed with oxygen, and sparked for a short time; it was then collected through the pump, which dried it, and it was remeasured. There was no contraction; the volume of the mixed gases *plus* added oxygen was 5·169 c.c., and that of the same gas after sparking 5·170 c.c. The amount of free hydrogen in air, therefore, must be less than $1/500$ of the volume of the combined neon and helium, assuming it to be possible to measure to 0·01 c.c. It should be added, perhaps, that it would be well not to regard this experiment as conclusive, but it is given for what it is worth.

*A New Radio-Active Element, which Evolves Thorium
Emanation. Preliminary Communication.*

By O. HAHN, Ph.D.

(Communicated by Sir William Ramsay, K.C.B., F.R.S. Received March 7,—
Read March 16, 1905.)

[The material for this investigation was provided by Sir William Ramsay ; it was the final residue remaining after fusion with bisulphate of 5 cwt. of the cubical ore from Ceylon, for which the name "thorianite" has been suggested by Professor Dunstan. This residue was fused with carbonates, the silica was removed, and the carbonates dissolved in dilute hydrochloric acid. Lead was precipitated as sulphide, and the carbonates again precipitated. These preliminary operations were carried out by Mr. Charles Tyrer and by Dr. Denison.]

This residue weighed about 18 grammes, and a preliminary estimation of radio-activity led to the belief that it would yield about 15 milligrammes of pure radium bromide. The carbonates were dissolved in pure aqueous hydrobromic acid, and the bromides fractionated according to Giesel's method. But difficulties were soon encountered; the more soluble portion did not fall off in radio-activity, but gradually grew more strongly radio-active; the radium concentrated at the least soluble end, and the middle fractions became relatively weak in radio-activity.

Small traces of iron and other impurities, unavoidable in London, collected in the more soluble portions, and the ferric bromide imparted to them a brownish-yellow colour. These, and indeed all fractions, were again treated with hydrogen sulphide, and a minute quantity of a peculiar dark-brown precipitate came down. It was also radio-active; it was soluble in nitric acid to a pale green solution, and on evaporation crystals of two kinds deposited; easily soluble green crystals and less soluble white ones. The investigation of these bodies is still in progress.

By a series of troublesome operations, a quantity of precipitate was obtained by aid of ammonia, and to separate iron, it was treated in acid solution with ammonium oxalate; this produced about 10 milligrammes of crystalline precipitate, which was by far the most active preparation obtained, and which shows after two months no diminution in its radio-active power. It glows feebly in the dark, and imparts bright luminosity to screens both of platino-cyanide and zinc sulphide. If a current of air be blown through a solution of this substance and directed on to a screen coated with zinc

sulphide, luminosity is produced, which, nevertheless, is different in intensity from that shown when a similar experiment is performed with Giesel's emanium. The phenomena are not so brilliant as those obtained from a strong sample of emanium kindly sent by Professor Giesel. It was not possible to perform the beautiful experiment of allowing the emanation to pour down on the screen and blowing it away, probably because the new substance emits β -rays in too great abundance. But that the dry substance also evolves emanation was easily discovered by help of an electrometer.

The first impression, that the new substance was identical with actinium or emanium, was found to be untenable,* for the new preparation evolves an emanation identical with that of thorium; different samples gave for the half-period of decay from 52 to 55 seconds; for the half-period of the induced activity, somewhat more than $11\frac{1}{2}$ hours was found, and a small remaining activity persists and decays very slowly. (The half-period for thorium emanation was found by Le Rossignol and Ginningham† to be 51.2 seconds; Bronson, working in Rutherford's Laboratory, found 54 seconds.) As this phenomenon has up till now not been noticed with thorium emanation, it may be conjectured either that another radio-active substance is mixed with the new body in very small traces, of which the induced radio-activity must have a long period of decay, or what is less probable, that the induced activity of thorium, like that of radium, changes into another product with a long radio-active existence. It is certain that radium emanation and also Rutherford's radium-E were absent.

The oxalate, which weighed 10 milligrammes, dissolved in hydrochloric acid, gave a quantity of emanation considerably greater than would be evolved from a kilogramme of thorium in solution; consequently, it is more than 100,000 times as active as thorium. Further work has resulted in the accumulation of 20 milligrammes of material nearly 250,000 times as active as its own weight of thorium nitrate. Thorium itself, if present at all, must be there in minimal quantity, for the oxalate gives tests for calcium for the most part. Whether this active substance is a constant radio-active constituent of thorium preparations, or whether it is another new radio-active element, remains still undecided. Its quantitative extraction from thorium salts has not yet been investigated. After precipitation of a small part of

* The measurements of the emanations and excited activities were carried out in collaboration with Dr. Sackur, working in this laboratory; we also re-determined the half-period of decay of the emanation from Giesel's emanium, as about three seconds, and for its induced activity a period of about 36 seconds. More exact measurements are in progress.

† 'Phil. Mag.,' July, 1904, p. 107.

the solution in hydrochloric acid of the original ammonia precipitate with ammonia, the filtrate shows considerable radio-activity, which rapidly falls off in a few days, but does not wholly disappear, and the removal of this substance does not diminish appreciably the radio-activity of the insoluble residue. Whether that is due to thorium— x or not has not yet been quantitatively investigated. The close relation of the new body to thorium is proved, not merely by the apparent identity of the two emanations, but also in its having been separated from a mineral unusually rich in thorium.*

We are in hopes that it may prove possible, by several processes of concentration, to obtain an even more strongly radio-active product, and to be able to describe more in detail the chemical properties of the substance; one difficulty consists in the adhesion of the substance to all precipitates; all filters are radio-active, and can hardly be purified by repeated washing. The activity of the sulphide precipitate may, perhaps, be due to this cause; the emanation which it yields appears to be identical with that obtained from the precipitate with ammonia.

Recent researches would appear to show that this substance is present in soil in amount comparable with, but still considerably smaller than radium. G. A. Blanc† has described in a paper on “the Radio-Activity of Mineral Springs,” a gas which contains thorium emanation. N. M. Dadourian,‡ in investigating the radio-activity of subterranean air, has detected not only radium emanation, but also that of thorium; and Elster and Geitel§ have described a preparation obtained from the mud from the Baden Baden “Ursprung” as containing no thorium in detectable quantity, but yet evolving thorium emanation in amount such that half a gramme of thorium oxide would be required to produce it. They conjecture, therefore, the presence of a new radio-active element. Attention may also be called to the fact that inactive thoria is said more than once to have been obtained.

It is almost certain that all these emanations are the product of this new substance, and are not derived from thorium itself, for the amount of emanation obtainable from thorium is so small that, if it can be measured at all, it should be possible to detect thorium analytically in the source from which it is evolved.

* Experiments are in progress in this laboratory to attempt to concentrate the radio-active substance from a large quantity of thorium; but, so far, no definite results have been obtained.

† ‘Phil. Mag.,’ vol. 9, pp. 148 to 154.

‡ ‘Sill. Amer. J. of Science,’ vol. 19, 1905, pp. 16 to 22.

§ “Radioaktivität der Sedimente der Thermalquellen,” ‘Chem. Centralbl.,’ 1905, vol. 1, p. 651.

*On the Spectrum of Silicon; with a Note on the Spectrum of
Fluorine.*

By JOSEPH LUNT, B.Sc., F.I.C.

(Communicated by Sir David Gill, K.C.B., F.R.S., H.M. Astronomer at the Cape
of Good Hope. Received February 13,—Read March 2, 1905.)

(PLATE 2.)

In a recent paper* M. A. de Gramont questions the silicon origin of certain lines, viz.: λ 4089.1, λ 4096.9, and λ 4116.4, grouped together as Group IV by Sir Norman Lockyer† who ascribes them to the element named. He says: “J’ajouterai que les lignes du groupe IV, qui indiqueraient, d’après Lockyer, une température excessive, ont toujours, sur mes clichés, accompagné les raies de l’air et ont disparu avec lui. Elles coïncident avec des lignes de l’oxygène et de l’azote, et ces deux gaz ont été reconnus dans plusieurs étoiles d’Orion et dans β *Crucis*. Je crois donc le groupe IV attribuable à l’air.”

Sir Norman Lockyer and Mr. Baxandall‡ have replied by bringing forward photographic evidence in support of their conclusions. Whilst agreeing with the latter authors that the lines in question, *with the exception of* λ 4096.9, are really silicon lines, I consider that the evidence brought forward by them is in itself insufficient to establish their conclusions satisfactorily.

Nearly three years ago I prepared a paper, “On the Spectrum of Silicon from its dissociated compounds,” for inclusion in vol. 10 of the ‘Annals of the Cape Observatory,’ but as this volume has not yet appeared, owing to other papers being still under preparation, it seems desirable to publish, in advance, an extract dealing particularly with the lines under present discussion and to mention briefly some other important lines. The extract is as follows:—

“*High-temperature lines $\lambda\lambda$ 4089.1 and 4116.4.*”

“These two lines were first recorded as silicon lines by Lockyer in his ‘Note on the Spectrum of Silicon,’§ and it is of great interest to notice their behaviour under different conditions. Of these lines Lockyer writes, ‘The

* ‘Comptes Rendus,’ vol. 139, p. 188.

† ‘Roy. Soc. Proc.,’ vol. 67, 1900, p. 405.

‡ ‘Roy. Soc. Proc.,’ vol. 74, 1904, p. 296.

§ ‘Roy. Soc. Proc.,’ vol. 65, p. 449.

lines in Group IV* have never been seen in the spark spectrum of silicium when small coil and small jar capacity are used,† but with the spark given by the Spottiswoode coil and plate condenser, they appear as weak lines. They are not, like the members of Groups II and III seen in the spectrum from the bulb when a vacuum tube is used, but in that given by the capillary the strongest ones are very prominent, and vie in intensity with the lines in Group III.'

"At the outset it may be stated that a large number of experiments had to be made before the confirmation of the silicon origin of these lines was considered satisfactory, but there can now be no doubt that Lockyer's identification is correct. These lines are absent in the list of lines given by Exner and Haschek, and by Eder and Valenta, and, so far as I know, no other observers have recorded them.

"In my earlier experiments with argon tubes‡ I had obtained these lines from the glass capillary, not only of argon tubes but also from those of other tubes containing various gases; and concluded that they may be obtained from glass vacuum tubes, whatever the gaseous contents may be, provided that sufficient jar capacity and a suitable spark gap are employed to decompose the glass. That I then doubted their silicon origin, however, is shown by the fact that they were not included in the list of silicon lines discussed in my first paper. This was owing to the fact that the spark spectrum of silicon tetra-fluoride had only been examined in wide tubes at atmospheric pressure, under which conditions the lines in question are absent, unless the immediate vicinity of the platinum electrodes is examined.

"I find that even at a pressure of 12.5 mm. the glass capillary of a silicon tetra-fluoride tube fails to give these lines when a small jar and gap are used, although the other silicon lines are very pronounced. If, however, the pressure be reduced to 3 mm., still using one small jar and gap, these lines come out strongly and are almost as strong as the strongest lines in the whole spectrum. With a similar pressure of silicon tetra-chloride, however, using the same jar and gap, these lines are exceedingly weak, whilst the rest of the silicon lines are strong.

"It is thus evident that the silicon spectrum from a mixture of silicon and chlorine (dissociated silicon tetra-chloride) is very different from that obtained from a similar mixture of silicon and fluorine (dissociated silicon

* Group IV consists of three lines, the two above, and one, λ 4096.9, which I do not obtain in my photographs, and regard its silicon origin as doubtful.

† I show later that small coil and jar capacity suffice to bring out these lines strongly in the spectrum from the capillary of tubes of the fluoride.

‡ 'Roy. Soc. Proc.,' vol. 66, p. 44.

tetra-fluoride). The effect of the chlorine being, apparently, to lower the temperature of the gas, and so extinguish the lines which require the highest temperature for their production.

"Lockyer* found that the presence of the chlorine in the dissociated chlorides of various metals had the effect of extinguishing the short, and therefore presumably high-temperature lines, for he writes: 'It was found, in all cases, that the difference between the spectrum of the chloride and the spectrum of the metal was: *That under the same spark conditions, the short lines were obliterated, while the air lines remained unchanged in thickness.* Changing the spark conditions by throwing the jar out of the circuit, this change was shown in its strongest form, the final results being that only the very longest lines in the spectrum of the metal remained.'

"This pronounced difference between the behaviour of silicon tetra-fluoride and silicon tetra-chloride had the effect of again throwing doubt on the silicon origin of the lines under discussion. On examining, however, the photographs taken for the purposes of the former paper, in which the spark spectrum had been taken in hydrogen from beads of sodium and potassium silicates made from rock-crystal, it was seen that these lines *did* occur as short lines close to the beads, but not extending throughout the spark, as did the other lines. This, in itself, was another evidence, not only of their silicon origin but also of the high temperature requisite for their production.

"All further doubt was, however, set at rest by preparing other beads of potassium silicate from carefully purified silica, made from silicic acid precipitated from silicon tetra-fluoride by water. The spectrum of these beads showed these lines as short lines as in the case of rock-crystal silicate, and their length was not much increased by sparking the beads in the fused state.

"Accordingly, the weakness or absence of these lines from the capillary of silicon tetra-chloride vacuum tubes was attributed to the above-mentioned effect of chlorine. These lines can, however, be obtained from silicon tetra-chloride tubes as strong lines, having much the same relative intensity as those obtained by Lockyer from the bromide, by increasing the number and size of jars and the width of the spark-gap; *but only at the expense of decomposing the glass of the tube itself.* This decomposition of the glass is evidenced by the appearance of a strong spectrum of oxygen and the almost complete obliteration of the chlorine spectrum, much in the same way as the spectra of argon and helium can be obliterated and replaced by those of silicon and oxygen. The spectrum thus obtained, is, in fact, practically identical with

* 'Phil. Trans.,' vol. 163 (1873), p. 256.

that obtained under similar conditions from a tube filled with pure oxygen at low pressure (2 mm.), residual air or any other gas, and cannot in any way be regarded as a spectrum of dissociated silicon tetra-chloride.

"A consideration of these facts suggests a serious objection to the acceptance of the spectrum obtained by Lockyer from a silicium bromide capillary vacuum tube by the use of the large Spottiswoode coil and plate condenser, as evidence that the lines in question are silicon lines. It is clear that they may be and probably are obtained from the glass tube and might equally well belong to some other material contained in it.

"For example, the H and K lines of calcium and the D lines of sodium, and even the strong triplet of manganese often accompany such spectra, and one might equally well attribute the lines to some other and possibly unknown substance.

"The weakness of the lines when obtained from silicon itself, a substance likely to contain impurities, as results show, and the fact that Exner and Haschek did not obtain them from the specimens of silicon with which they worked, would rather suggest that they were due to some impurity in Lockyer's specimen of silicon; the fact of obtaining them as such strong lines from a silicium bromide capillary vacuum tube, under the conditions of his experiments is no evidence to the contrary.

"Such evidence must, in fact, be obtained from carefully prepared pure silicates, or other pure silicon compounds, *sparked under such conditions that the presence of glass cannot possibly vitiate the results.* These two lines are present in ϵ Canis Majoris and other helium stars, as strong lines, together with other silicon lines, but the low-temperature silicon lines are either absent or very weak, the only low-temperature lines present in ϵ Canis Majoris being the persistent pair 4128 and 4131, which are weak and indistinct lines."

The photographs presented by Lockyer and Baxandall only serve to confirm the views expressed in the foregoing extract, viz.: that the silicon lines from their vacuum tubes filled with gaseous silicon compounds have their origin as much in the material of the glass capillary as in the gaseous compound introduced, and if we had no other evidence to the contrary, we might equally well say that the lines of calcium, sodium, and manganese, which appear in vacuum tubes so filled, belong to silicon and not to the metals named.

The spectra of silicon tetra-fluoride vacuum tubes reproduced in their paper show a very strong spectrum of oxygen, which is sufficient evidence

that the spark conditions were such as to result in the decomposition of the glass of the tube, which introduces great uncertainty as to the nature of all the materials thus rendered incandescent. The oxygen lines cannot be due to contamination with atmospheric air, as the spectrum of nitrogen is absent.

The photographs of spectra which accompany this note, show clearly the unimportant part played by the silicon tetra-fluoride in the production of the silicon lines in Lockyer and Baxandall's photographs, as their spectrum is practically identical, except for the presence of a few fluorine lines, with the second strip of the photographs sent herewith, which was produced from an oxygen tube, and could have been equally well obtained from a tube containing argon, helium or other gases under suitable conditions (Plate 2).

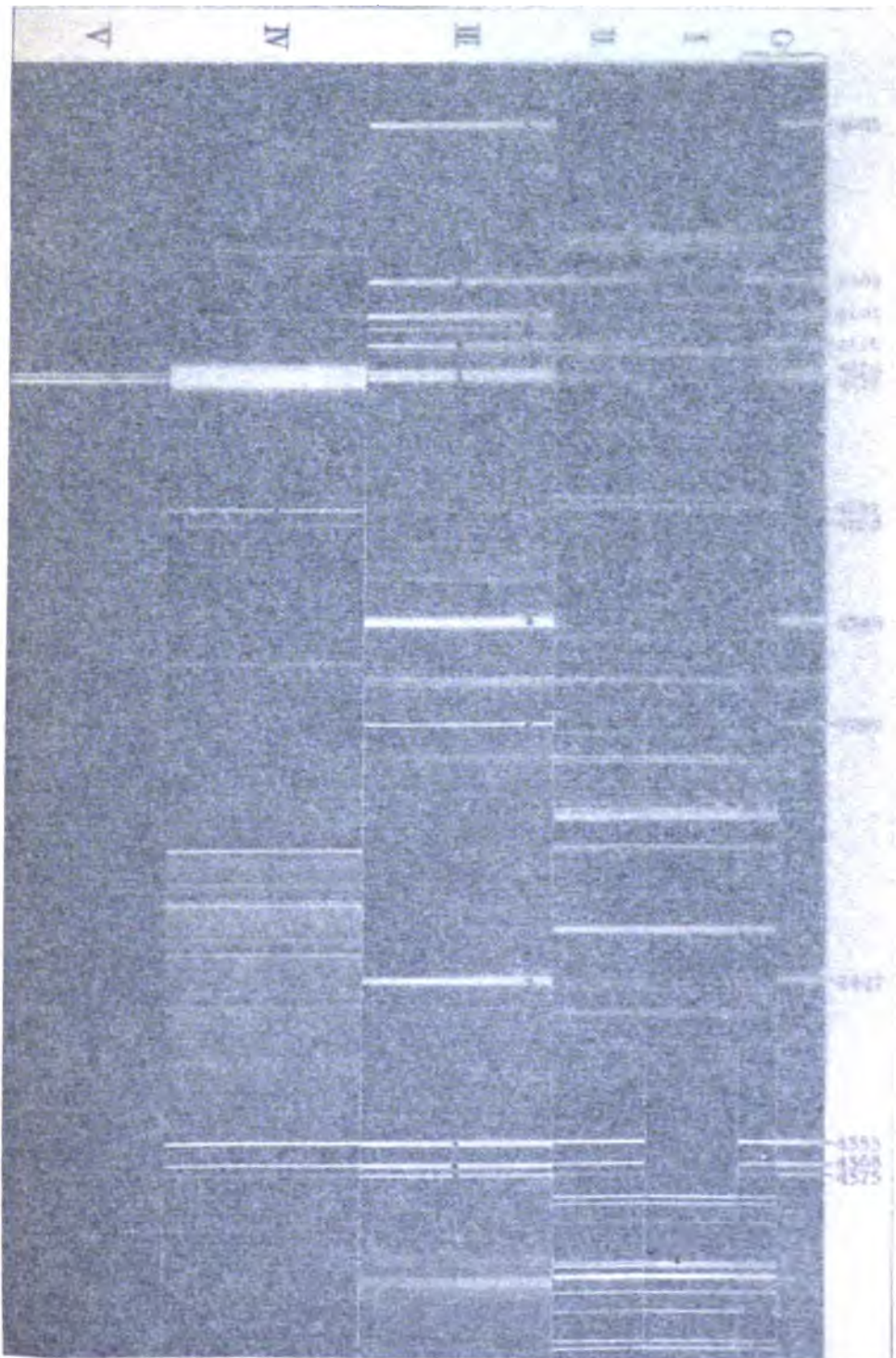
The first strip shows the spectrum of oxygen for comparison. It was taken from the same tube as the second strip, but with small coil and small jar instead of the heavy disruptive discharge from the large coil and four large jars. The third strip shows, however, that a *true* spectrum of dissociated silicon tetra-fluoride may be obtained without simultaneously producing a strong oxygen spectrum. This is a spectrum of the gaseous materials purposely introduced into the tube, and not one of the glass of the tube itself, and therefore it has far more value as evidence, especially in view of M. de Gramont's statement that the lines of Group IV, in his experiments, appear and disappear with the air lines.

This photograph was produced with a small coil and a small jar, which gave a discharge insufficient to decompose the glass capillary. It will be seen that the spectrum of oxygen is almost completely eliminated, a trace only of the strongest lines, the strong triplet mentioned by Lockyer and Baxandall, being just perceivable.

The two strong lines of Lockyer's Group IV are, however, amongst the strongest in the spectrum, and they are accompanied by the well known pair $\lambda\lambda$ 4128 and 4131 in Group II and the strong triplet of Group III. *

Moreover the spectrum of fluorine, considered later, is much stronger than in the Kensington spectra. The strongest fluorine lines are marked with one black dot at the upper end, whilst the silicon lines are marked by one black dot in the middle, the wide pair of silicon lines to the left being the two strong lines of Lockyer's Group IV, λ 4089 and λ 4116, the close pair on their right belonging to his Group II, λ 4128 and λ 4131,

* Sir Norman Lockyer and myself almost simultaneously and independently discovered these strong stellar lines (Group III) to be due to silicon, but both of us had not noticed that M. de Gramont had previously recorded them as silicon lines, which he found in the spectra of silicates ('Comptes Rendus,' vol. 124, p. 192).



the spectrum of the gas evolved in the decomposition of the compound, and is as creamy as to the nature of all the lines present. The oxygen lines cannot be seen, and the spectrum is the spectrum of nitrogen as before.

These experiments, which I have already noted, show clearly the necessity of using a large coil and a large jar in the production of the spectrum of silicon. The small apparatus, as their spectrum is practically identical with that of oxygen, a few fluorine lines, with the small jar, and the spectrum which was produced from an oxygen tube, is not obtained from a tube containing silicon under the same conditions (Plate 2).

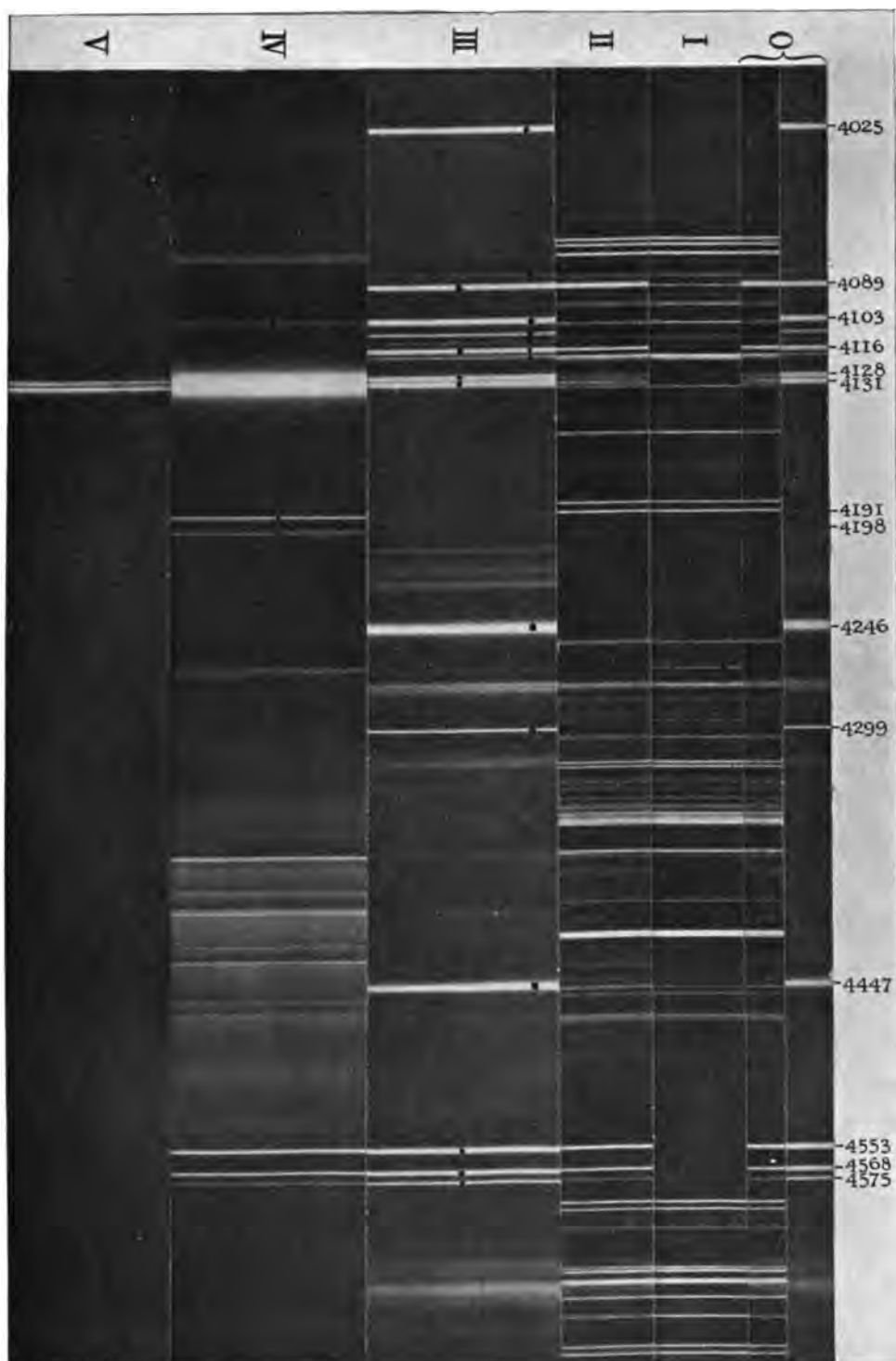
The spectrum of the gas evolved for comparison. It was produced with small coil and small jar, and the spectrum from the large coil and four jars, which is a true spectrum of dissociated silicon, without simultaneously producing a spectrum of the gaseous materials purposely evolved. The spectrum of the glass of the tube itself, and the spectrum of the gas evolved, is evidence, especially in view of M. de Lockyer's results of Group IV, in his experiments, appear to be identical.

The spectrum of the gas evolved with a small coil and a small jar, which is a true spectrum of silicon, is almost completely eliminated, a trace of the strongest lines, the strong triplet mentioned by Lockyer and being just perceptible.

Two strong lines of Lockyer's Group IV are, however, amongst the strongest in the spectrum, and they are accompanied by the well known lines λ 4128 and λ 4131 in Group II and the strong triplet of Group III. *

The spectrum of fluorine, considered later, is much stronger than that of silicon. The strongest fluorine lines are marked with the strongest lines of silicon, whilst the silicon lines are marked by one of the strongest lines of fluorine, the wide pair of silicon lines to the left being the strongest lines of fluorine. Lockyer's Group IV, λ 4089 and λ 4116, the strongest lines of fluorine, belonging to his Group II, λ 4128 and λ 4131.

* The spectrum of fluorine was most simultaneously and independently discovered than that of silicon, but both of us had not noticed that the lines of fluorine were due to fluorine as silicon lines, which he found in the spectrum of fluorine (Lockyer, *Phil. Mag.*, 1868, 192).



and the strong triplet on the right being Group III, λ 4553, λ 4568, and λ 4575.

Strip IV shows the central part of a negative taken from a silicon tetra-fluoride capillary under conditions which leave part of the SiF_4 undecomposed, as the band spectrum of this compound (mentioned also by Eberhard) shows. In this the fluorine lines are practically absent, although the silicon lines are very strong.

All the 12 lines * (Group IV being absent) of Lockyer's first three groups are exceedingly distinct, as well as two lines, the pair to the right of the very strong pair λ 4128 and λ 4131, which I regard as two new silicon lines not hitherto recorded by any who have worked on the spectrum of silicon.

Strip V shows the pair 4128, 4131 as intense as in strip III, but without the lines of Groups III and IV. It is interesting as representing the low-temperature stellar spectrum of silicon reproduced in the laboratory. It is from a silicon tetra-chloride vacuum tube.

Herr G. Eberhard† has also made an important investigation of the spectra of silicon obtained from its halogen compounds, he says: "The arc lines λ 3905 and λ 4103 occur throughout the spark, but the lines λ 4089 and λ 4116 on the contrary occur only in the immediate neighbourhood of the points of the electrodes," which agrees with the results of my experiments with silicates mentioned in the preceding extract, and probably explains why Exner and Haschek missed these lines, as Eberhard points out.

The wave-length of the silicon line 4116 cannot be accurately measured in presence of a strong fluorine spectrum unless sufficient dispersion is employed to separate the slightly less refrangible fluorine line.

I have hitherto left out of account the middle line of Lockyer's Group IV, viz.: λ 4096.9. It is a very important stellar line as the following extract from Cannon and Pickering's‡ intensities show.

	29 Can. Maj.	τ Can. Maj.	ϵ Orionis.	β Centauri.	γ Orionis.
4089.2§.....	6	12	15	5	2
4096.9	18	6	4	2	1
4101.8 H_δ	25	25	25	35	40
4116.2	3	6	10	2	0

* The green pair 5042, 5057, the arc line 3906, and the Group II triplet 3854, 3856, and 3863 are outside the limits of the strip sent for reproduction.

† 'Zeitschrift für Wissenschaftliche Photographie, Photophysik und Photochemie,' Band 1, Heft 10, 1903, p. 349.

‡ 'Annals of the Observatory of Harvard College,' vol. 28, part 2, pp. 233 and 235.

§ The first and last of these are silicon lines. Cannon and Pickering assign no origin.

They say: "4096.9 is so near H_β wave-length 4101.8 that it gives the hydrogen line the appearance of being double, or of having a bright central line superposed on a broad dark line. By superposing this spectrum upon that of another star, it is easily seen that H_β is not double.

"It then appears that H_β of the superposed image matches the line of greater wave-length in this spectrum and the line 4096.9 is well separated from the hydrogen line. 4096.9 has not been seen in the preceding classes of spectra, and is strongest in spectra of this class (viz., Oe) declining in intensity in succeeding classes until B_3A is reached, when it is not present."

It is doubtless the same line that Lockyer* records as λ 4097.3 in ϵ Orionis, ascribing its origin to Si (IV), and Hartmann† in δ Orionis as λ 4097.49, he also ascribing it to silicon, following Lockyer and Exner and Haschek as regards origin. Exner and Haschek find its wave-length as 4096.8, whilst A. de Gramont places a line at λ 4097.3, but ascribes it to air. Eberhard does not mention any silicon line here.

This line is certainly not present in the purest silicon spectra which I have been able to obtain and which show the other two lines of Group IV strongly. In strip III of the accompanying photographs its place lies between the silicon line 4089 and the fluorine line 4103, a region destitute of lines of any kind.

In 29 Can. Maj., according to Cannon and Pickering, this line is three times as intense as the stronger silicon line of Group IV, but—as is shown in the preceding extract from their intensities—it becomes weaker in stars showing the Group IV lines of silicon more strongly. I am convinced, therefore, not only because of the absence of this line in strip III and its relative weakness in the spectra of both Lockyer and Exner and Haschek, but also because of stellar evidence, that some other origin than silicon must be sought for this line.

There are both oxygen and nitrogen lines very close to this place, but neither of these elements account for the strong stellar line. These elements are sufficient, however, to account for the line in laboratory spectra of silicon showing air lines.

Exner and Haschek's lines 3883.46, 4021.0 and 4764.20.—These lines do not appear in the Cape photographs. Neither Lockyer nor Eberhard finds them and M. A. de Gramont does not mention them. They also should be struck out from the list of silicon lines, as due to accidental impurities.

Line λ 4030.—Similarly with line λ 4030, found both by Exner and Haschek and Lockyer, although Lockyer states that it may be due to an

* 'Catalogue of 470 of the Brighter Stars' (1902), p. 52.

† 'Astrophysical Journal,' vol. 19, p. 272.

impurity, and he does not include it in any of his four groups. This line is not obtained either by Eberhard or myself, and should also be struck out.

Lines λ 3854 and λ 4103.—The lines 3853.9 and 4103.2 of Lockyer, which Eberhard does not obtain, are present in the Cape photographs, whilst Exner and Haschek record them as double lines. I do not doubt the silicon origin of these lines, but find them to be single and not double. The latter line is involved with both fluorine and oxygen lines when the spectra of those elements are present, but it is seen both in the spectra of the chloride and fluoride of silicon when examined under conditions which preclude the presence of the halogen spectra.

Mention may also be made of two pairs of silicon lines, one in the orange and another in the red, which were first noted by A. de Gramont. These I have confirmed, as well as the green pair also noted by A. de Gramont and confirmed by Lockyer.

New pair of Silicon Lines.—There is, however, another pair of lines which have not hitherto been recorded, which I regard as low-temperature silicon lines. Their wave-lengths are λ 4191.0 and λ 4198.5; they are well shown in strip IV. On the same negative are six other low-temperature lines, viz.: λ 3854, λ 3856, λ 3863, λ 3906 and the green pair λ 5042 and λ 5057. The pair λ 4128 and λ 4131 is very strong in the photograph (strip IV) whilst λ 4103 is a weak line.

The banded spectrum of the undecomposed fluoride is also well shown. This *partial* dissociation of the gas is evidence of the low-temperature condition, and the absence of the fluorine lines is well marked.

This new pair of lines was also obtained in the chloride, both in capillary tubes, at pressures of from 3.5 to 12.5 mm., and also in the spark between platinum electrodes in a bulb filled with the vapour of the chloride at atmospheric pressure.

Note on the Spectrum of Fluorine.

It is a remarkable fact that none of the observers who have worked with the spectrum of silicon tetra-fluoride have attempted to assign a definite spectrum to fluorine, although its lines must have accompanied most of their silicon spectra. It is also remarkable that Lockyer and Baxandall's Plate 11, strip A, shows the strongest fluorine lines clearly differentiated from the oxygen and silicon lines by being thickened in the lower half of the strip. Notice particularly the line beneath the letter V in Vacuum Tube.

None of the silicon and oxygen lines have this appearance, and the following

lines may be picked out in their photograph by mere inspection, viz. : λ 4103 λ 4109, λ 4246, λ 4299, and λ 4447.

The further elucidation of this interesting spectrum is suggested as a fruitful field for further research, which might preferably be undertaken outside an astronomical observatory.

It is evident that a complete knowledge of the spectrum of fluorine will help to increase our knowledge of the spectrum of silicon, and probably that of other elements which have volatile fluorides.

There is a fluorine line on the green side of the 4116 silicon line with a wave-length of $\pm \lambda$ 4116.8, stronger than the fluorine line 4113 and fainter than 4119, which in spectra of dissociated silicon tetra-fluoride gives the silicon line too high a value for wave-length, unless sufficient dispersion is employed to separate the two lines.

A list of lines which may be ascribed to fluorine is appended. There are other lines in this region which may be due either to silicon or fluorine, but further experiments are necessary before their origin can be determined satisfactorily.

Spectrum of Fluorine.

	λ .	Intensity.		λ .	Intensity.
1st Triplet	3847.3	3	Group of five lines	4103.6	10
	3850.2	2		4109.3	5
	3851.8	1		4113.0	2
2nd Triplet	3899.0	2		4116.8	2
	3902.1	1		4119.3	3
	3904.0	< 1		4246.5	30
	4025.3	10 du ?		4299.3	7
	4084.1	2		4446.8	20

The Basic Gamma-Function and the Elliptic Functions

By the Rev. F. H. JACKSON, R.N.

(Communicated by Professor A. R. Forsyth, Sc.D., LL.D., F.R.S. Received November 12,—Read December 15, 1904.)

Introduction.

In this paper I propose to discuss certain product functions.

- I. Functions of which the typical factor is $[x+n\omega]$, that is to say $(p^{x+n\omega}-1)/(p-1)$.
- II. Functions of which the typical factor is $[x+m\omega_1+n\omega_2]$.

The functions belonging to the first class are substantially the q products, which appear in Elliptic Function theory. Many different notations have been used in the discussion of such functions, notably the notations of Jacobi, Weierstrass, Halphen, Tannery, and Molk. Halphen* discusses the notations used by various writers, and compares their respective advantages. In the following work the products will be discussed under a notation analogous to that of the gamma-function. The function $\Gamma_p(x, \omega)$, which will be used is the simplest function satisfying the difference equation

$$f(x+\omega) = [x]f(x), \quad (A)$$

p is termed the base, and ω is termed the parameter of the function. In case $p = 1$, the function $\Gamma_p(x, \omega)$ degenerates into the gamma function with parameter ω .

From $\Gamma_p(x, \omega)$ a function $S_p(x, \omega)$ will be derived.

$$S_p(x, \omega) = \frac{\lambda}{\Gamma_p(\omega-x) \Gamma_p(x)}.$$

It is manifest that when $p = 1$, this function will degenerate into $\sin \pi x/\omega$, also that for special values of p it will differ from the σ functions only by an exponential factor of the second degree. Functions of this nature are discussed by Halphen.†

In the discussion of the products with a typical factor $[x+m\omega_1+n\omega_2]$, functions $G_p(x, \omega)$ and $G_p(x, \omega_1, \omega_2)$ analogous to the G function and the double-gamma function will be formed, and from these, certain functions denoted $T_p(x, \omega)$, $\tau(x, \omega_1, \omega_2)$ will be derived, satisfying difference equations for the ω parameters, with elliptic function coefficients.

* 'Fonctions Elliptiques,' vol. 1, p. 252.

† 'Fonctions Elliptiques,' vol. 1, pp. 240, et seq.

For general investigations of q series, not specially in connection with Elliptic Function theory, I refer to Heine,* to memoirs† by Professor L. J. Rogers, and to sundry papers‡ by the author.

It may be useful to state here the principal transformations which appear in this paper.

$$\begin{aligned}\Gamma_p\left(x, \frac{\omega}{n}\right) &= \text{const.} \prod_{r=0}^{n-1} \left\{ \Gamma_p\left(x + \frac{r\omega}{n}, \omega\right) \right\}, \\ S_p\left(x, \frac{\omega}{n}\right) &= \text{const.} \prod_{r=0}^{n-1} \left\{ S_p\left(x + \frac{r\omega}{n}, \omega\right) \right\}, \\ Z_p\left(x, \frac{\omega}{n}\right) &= \sum_{r=0}^{n-1} \left\{ Z_p\left(x + \frac{r\omega}{n}, \omega\right) \right\}, \\ \Phi_p\left(x, \frac{\omega}{n}\right) &= \sum_{r=0}^{n-1} \left\{ \Phi_p\left(x + \frac{r\omega}{n}, \omega\right) \right\}, \\ G_{p,n}^{\frac{1}{2}}(nx, \omega) &= \lambda C^x \left[\frac{1}{n} \right]^{-nx(nx-\omega)} \prod_{r=0}^{n-1} \prod_{s=0}^{n-1} \left\{ G_p\left(x + \frac{r+s}{n} \omega, \omega\right) \right\}, \\ T_{p,n}^{\frac{1}{2}}(nx, \omega) &= C^x \left[\frac{1}{n} \right]^{n^2x^2/\omega^2} \prod_{r=0}^{n-1} \prod_{s=0}^{n-1} \left\{ T_p\left(x + \frac{r+s}{n} \omega, \omega\right) \right\}.\end{aligned}$$

1.

Function $\Gamma_p(x, \omega)$.

In order to bring the function $\Gamma_p([x])$ § into line with more general products, we introduce a parameter, ω , and form a function satisfying the difference equation

$$f(x+\omega) = [x]f(x),$$

and such that

$$\Gamma_p(\omega, \omega) = 1.$$

The function is

$$\Gamma_p(x, \omega) = \frac{1}{[x]_{x=\infty}} \mathbb{L} \frac{[\omega][2\omega][3\omega] \dots [\kappa\omega]}{[x+\omega][x+2\omega][x+3\omega] \dots [x+\kappa\omega]} [\kappa\omega]^{x/\omega}, \quad (1)$$

in which

$$|p^\omega| < 1.$$

The infinite product is also convergent when $|p^\omega| > 1$, but the function does not then satisfy the difference equation $f(x+\omega) = [x]f(x)$. By introducing, however, an exponential factor, $p^{x(x+\omega)/2\omega}$, we have, in case $|p^\omega| > 1$, a function

* 'Kugelfunctionen,' chap. 2, vol. 1, Appendix.

† 'London Math. Socy. Proc.,' vols. 24 and 25.

‡ 'London Math. Socy. Proc.,' series 2, vols. 1, 2, and 3; 'R. S. Edin. Trans.,' vol. 41; 'Amer. Jour. Math.,' vol. 27.

§ 'Roy. Soc. Proc.,' vol. 74, p. 61.

$$\Gamma_p(x, \omega) = \frac{1}{[x]} \mathbf{L}_{\infty} \frac{[\omega][2\omega][3\omega] \dots [\kappa\omega]}{[x+\omega][x+2\omega] \dots [x+\kappa\omega]} [\kappa\omega]^{x/\omega} p^{x(x+\omega)/2\omega}, \quad (1, a)$$

which satisfies the difference equation (A). In terms of the function $\Gamma_p([x])$,* we find

$$\Gamma_p(x, \omega) = [\omega]^{(x/\omega)-1}$$

analogous to

$$\Gamma_1(x, \omega) = \omega^{(x/\omega)-1} \Gamma(x/\omega). \dagger$$

It is easily deduced that

$$\Gamma_p(-x, -\omega) = -p^x e^{2\pi i x/\omega} \Gamma_p(x, \omega).$$

The function (1) may be expressed in other forms, for example,

$$\begin{aligned} \frac{1}{\Gamma_p(x, \omega)} &= [x] (1-p)^{x/\omega} \prod_{s=1}^{\infty} \frac{[x+s\omega]}{[s\omega]} \\ &= [x] (1-p)^{x/\omega} \prod_{s=1}^{\infty} \left\{ 1 + p^{s\omega} \frac{[x]}{[s\omega]} \right\}. \end{aligned} \quad (B)$$

These expressions are absolutely convergent of $|p^\omega| < 1$, but they are not convergent in case $p = 1$. We can, however, form an expression convergent in this limiting case, viz.:—

$$\begin{aligned} \frac{1}{\Gamma_p(x, \omega)} &= e^{-Qx} [x] \prod_{s=1}^{\infty} \left\{ \left(1 + p^{s\omega} \frac{[x]}{[s\omega]} \right) e^{-\frac{p^{s\omega}}{[s\omega]}} \right\}. \quad (C) \\ Q &= \frac{1}{\omega} \log \frac{1}{1-p} - \sum_{s=1}^{\infty} \frac{p^{s\omega}}{[s\omega]} \end{aligned}$$

A similar expression in case $|p^\omega| > 1$, is easily written down. As p approaches the value unity from either side, the two expressions converge into a limiting form, viz., Weierstrass' expression for the gamma-function.

Multiplication Theorem and Transformation of the Parameter ω .

Consider
$$\phi(x) = \frac{\Gamma_p^{\frac{1}{n}}(nx, \omega)}{\prod_{r=0}^{n-1} \left\{ \Gamma_p \left(x + \frac{r\omega}{n}, \omega \right) \right\}} \left[\frac{1}{n} \right]^{nx/\omega}.$$

Then, since

$$\Gamma_p^{\frac{1}{n}}(nx + n\omega, \omega) = \frac{\left[x + \frac{n-1}{n} \omega \right]}{\left[\frac{1}{n} \right]} \Gamma_p^{\frac{1}{n}}(nx + (n-1)\omega, \omega),$$

we find

$$\phi(x + \omega) = \phi(x).$$

The function $\phi(x)$ has no singularities when x is positive, it is finite and

* 'Roy. Soc. Proc.', vol. 74, p. 61.

† Cf. Barnes, 'Messenger of Mathematics,' 1899, p. 71.

single-valued since only principal values of $[x]$ are denoted by that symbol, therefore, by Lionville's theorem, $\phi(x)$ is constant, and by putting $x = \frac{\omega}{n}$, we are able to write

$$\Gamma_p^1(nx, \omega) = \frac{\left[\frac{1}{n}\right]^{1-\frac{nx}{\omega}}}{\prod_{r=0}^{n-1} \left\{ \Gamma_p\left(\frac{r\omega}{n}, \omega\right) \right\}} \prod_{r=0}^{n-1} \left\{ \Gamma_p\left(x + \frac{r\omega}{n}, \omega\right) \right\}, \quad (6)$$

which is a quasi-multiplication theorem for the function $\Gamma_p(x, \omega)$, reducing to the multiplication theorem of Gauss and Legendre in case $p=1, \omega=1$.

It is easily shown that

$$\Gamma_p^1(nx, \omega) = \left[\frac{1}{n}\right]^{1-\frac{nx}{\omega}} \Gamma_p\left(x, \frac{\omega}{n}\right). \quad (7)$$

If we apply this to equation (6), it reduces that equation to the form

$$\Gamma_p\left(x, \frac{\omega}{n}\right) = C \prod_{r=0}^{n-1} \left\{ \Gamma_p\left(x + \frac{r\omega}{n}, \omega\right) \right\}, \quad (8)$$

in which

$$C = \prod_{r=1}^n \left\{ \Gamma_p\left(\frac{r\omega}{n}, \omega\right) \right\}^{-1}.$$

Denoting the derivatives of $\log \Gamma_p(x, \omega)$ by $\psi_p(x, \omega)$, it is seen that

$$\psi_p^{(n)}\left(x, \frac{\omega}{n}\right) = \sum_{r=0}^{n-1} \psi_p^{(n)}\left(x + \frac{r\omega}{n}, \omega\right). \quad (9)$$

These expressions form transformation theorems for $\Gamma_p(x, \omega)$ and its logarithmic derivatives.

2.

Function $S_p(x, \omega)$.

Consider the absolutely convergent product

$$f(x) = \lambda [x] \left\{ \frac{[\omega+x][\omega-x]}{[\omega]^2} \right\} \left\{ \frac{[2\omega+x][2\omega-x]}{[2\omega]^2} \right\} \dots, \quad (10)$$

which reduces, in case $p=1$, to $\lambda \sin \frac{\pi x}{\omega}$. The product may be expressed by

(1) as

$$\frac{\lambda}{\Gamma_p(x, \omega) \Gamma_p(\omega-x, \omega)}.$$

Choose $\lambda^{\frac{1}{2}} = \Gamma_p\left(\frac{\omega}{2}, \omega\right)$, and now denote the function by the symbol

$$S_p(x, \omega).$$

It is at once evident that

$$S_p(0, \omega) = 0, \quad S_p\left(\frac{\omega}{2}, \omega\right) = 1;$$

also by means of the difference equation of the Γ_p function

$$\frac{S_p(x+\omega)}{S_p(x)} = \frac{[-x]}{[x]} = -p^{-x},$$

so that
$$S_p(x+2m\omega) = p^{-2mx-m(2m-1)\omega} S_p(x). \quad (11)$$

Transformation of the Parameter ω .

It has been shown that

$$\Gamma_p\left(x, \frac{\omega}{n}\right) = C \prod_{r=0}^{n-1} \left\{ \Gamma_p\left(x + \frac{r\omega}{n}, \omega\right) \right\},$$

therefore

$$\begin{aligned} \Gamma_p\left(x + \frac{\omega}{n}, \frac{\omega}{n}\right) &= \left(-x + \frac{\omega}{n}, \frac{\omega}{n}\right) \\ &= C^2 \prod_{r=0}^{n-1} \left\{ \Gamma_p\left(x + \frac{(r+1)\omega}{n}, \omega\right) \Gamma_p\left(-x + \frac{(r+1)\omega}{n}, \omega\right) \right\} \\ &= C^2 \prod_{r=0}^{n-1} \left\{ \Gamma_p\left(x + \frac{r\omega}{n}\right) \Gamma_p\left(\omega - x - \frac{r\omega}{n}\right) \right\} \Gamma_p(\omega+x) \Gamma_p(\omega-x). \quad (12) \end{aligned}$$

Since
$$S_p(x, \omega) = \frac{\lambda[x]}{\Gamma_p(\omega+x) \Gamma_p(\omega-x)} \quad \text{and} \quad \lambda^{\frac{1}{2}} = \Gamma_p\left(\frac{\omega}{2}, \omega\right),$$

we are able to write this equation (12)

$$S_p\left(x, \frac{\omega}{n}\right) = A \cdot S_p(x, \omega) S_p\left(x + \frac{\omega}{n}, \omega\right) \dots S_p\left(x + \frac{(n-1)\omega}{n}, \omega\right). \quad (13)$$

$$A = \left\{ \frac{\Gamma_p\left(\frac{\omega}{2n}, \frac{\omega}{n}\right)}{\Gamma_p\left(\frac{\omega}{2}, \omega\right)} \right\} \left\{ S_p\left(\frac{\omega}{n}, \omega\right) S_p\left(\frac{2\omega}{n}, \omega\right) \dots S_p\left(\frac{(n-1)\omega}{n}, \omega\right) \right\}^{-1}.$$

We notice that

$$\Gamma_p\left(\frac{\omega}{2}, \omega\right) = (1-p^\omega)^{\frac{1}{2}} \prod_{i=1}^{\infty} \frac{1-p^{i\omega}}{1-p^{i-\frac{1}{2}}\omega} = 1 + \frac{1}{2}p^\omega + p^{3\omega/2} + \dots$$

Denoting the first derivative of $\log S_p(x, \omega)$ by $Z_p(x, \omega)$, and the second derivative by $\Phi_p(x, \omega)$, it follows that

$$\begin{aligned} Z_p\left(x, \frac{\omega}{n}\right) &= \sum_{r=0}^{n-1} Z_p\left(x + \frac{r\omega}{n}, \omega\right) \\ \Phi_p\left(x, \frac{\omega}{n}\right) &= \sum_{r=0}^{n-1} \Phi_p\left(x + \frac{r\omega}{n}, \omega\right) \end{aligned} \quad (14)$$

* Cf. Halphen, 'Fonctions Elliptiques,' vol. 1, p. 196.

From the infinite product expression for $\Gamma_p(x, \omega)$ it follows that

$$\Gamma_p(\lambda x + 1, 1) \Gamma_p(1 - \lambda x, 1) = \prod_{m=1}^{\infty} \frac{(1 - q^{2m})^2}{\{1 - q^{2m}(q^{2\lambda x} + q^{-2\lambda x}) + q^{4m}\}}. \quad (15)$$

It is easily deduced that

$$\left. \begin{aligned} S_p\left(\frac{x}{2\omega_2}, 1\right) &= \frac{\pi}{\omega_1} (q^2 - 1)^{-1} \Gamma_p^2\left(\frac{1}{2}\right) e^{\frac{i\pi}{2} - \frac{(i\pi x - \eta_1 x^2)}{2\omega_1}} \sigma(x), \\ Z_p\left(\frac{x}{2\omega_2}, 1\right) &= \frac{i\pi\omega_2}{\omega_1} - \frac{2\eta_1\omega_2 x}{\omega_1} + 2\omega_2 \zeta(x), \\ \Phi_p\left(\frac{x}{2\omega_2}, 1\right) &= -\frac{4\eta_1\omega_2^3}{\omega_1} + 4\omega_2^3 \wp(x). \end{aligned} \right\} \quad (16)$$

Various series expressions for the functions S , Z , and ϕ may be obtained, either directly from their forms given above, or from known series in connection with the functions σ , S , \wp or the functions \mathfrak{J}_1 , \mathfrak{J}_2 , \mathfrak{J}_3 of Halphen's Treatise:—

$$\text{Since} \quad \frac{S_p(x, \omega)}{S_p(y, \omega)} = \frac{\Gamma_p(y) \Gamma_p(\omega - y)}{\Gamma_p(x) \Gamma_p(\omega - x)}, \quad (17)$$

and the quotient of the basic-gamma functions may be expanded in a Heinean series.†

$$1 + p^y \frac{[\omega - y - x][x - y]}{[x][\omega - y]} + p^{2y} \frac{[\omega - y - x][2\omega - y - x][x - y][x - y + \omega]}{[\omega][2\omega][\omega - y][2\omega - y]},$$

$$\text{also} \quad S_p\left(\frac{\omega}{2}, \omega\right) = 1,$$

it follows that

$$S_{p^2}^{-1}(x, \omega) = 1 + p^x \frac{[\omega - 2x][2x - \omega]}{[\omega][2\omega]} + p^{2x} \frac{[\omega - 2x][2\omega - 2x][2x - \omega][2x + \omega]}{[\omega][2\omega][3\omega][4\omega]}. \quad (18)$$

Similarly,

$$S_{p^2}^{-1}(x, \omega) = 1 + p^{2x} \frac{[\omega - 2x]^2}{[2\omega][2\omega - 2x]} + \dots$$

and by taking account of the expression

$$S_p\left(\frac{x}{2\omega_2}, 1\right) = A e^{ax + bx^2} \sigma(x),$$

in which $q = e^{i\pi\omega_2/\omega_1}$, we find

$$\frac{e^{\frac{i\pi}{2\omega_1}(x-y) - \frac{\eta_1}{2\omega_1}(x^2 - y^2)} \sigma(x)}{\sigma(y)} = 1 + p^{\frac{y}{\omega_2}} \frac{\left[2 - \frac{y+x}{\omega^2}\right]}{\left[2\right] \left[2 - \frac{y}{\omega_2}\right]} + \dots \quad (19)$$

* Cf. Halphen, vol. 1, p. 393.

† 'Amer. Journal Math.', vol. 27, p. 1.

3.

Series involving q Forms of Bessel's and Legendre's Coefficients.

I have shown* that

$$\begin{aligned}(1-x)_n &= L \frac{(1-x)(1-px) \dots (1-p^n x)}{(1-p^0 x)(1-p^{n+1} x) \dots (1-p^{n+n} x)} \\ &= 1 - \frac{[n]}{[1]} x + p \frac{[n][n-1]}{[2]!} x^2 - \dots \\ &\quad (-1)^r p^{r(r-1)} \frac{[n][n-1] \dots [n-r+1]}{[r]!} x^r + \dots, \\ &\quad (|p| < 1).\end{aligned}$$

Changing the base p into p^2 , and replacing x by $p^2 x \lambda$, we write

$$\begin{aligned}(1-p^2 x \lambda)_{-1} &= \prod_{m=1}^{\infty} \frac{(1-p^{2m} \lambda x)}{(1-p^{2m-1} \lambda x)} = 1 - \frac{[-1]}{[2]} p^2 x \lambda + p^2 \frac{[-1][-3]}{[2][4]} p^4 x^2 \lambda^2 \\ &\quad - \dots \\ &= \left\{ 1 + p x \lambda \frac{[1]}{[2]} + p^2 x^2 \lambda^2 \frac{[1][3]}{[2][4]} + \dots + p^r x^r \lambda^r \frac{[1] \dots [2r-1]}{[2][4] \dots [2r]} + \dots \right\}.\end{aligned}$$

Writing $\lambda = e^{2i\theta}$, we have

$$\begin{aligned}(1-p^2 x e^{2i\theta})_{-1} \times (1-p^2 x e^{-2i\theta})_{-1} &= (1-2p^2 x \cos 2\theta + p^4 x^2)_{-1} \\ &= \prod_{m=1}^{\infty} \frac{(1-2p^{2m} x \cos 2\theta + p^{4m} x^2)}{(1-2p^{2m-1} x \cos 2\theta + p^{4m-2} x^2)} \\ &= \left\{ 1 + p + \lambda \frac{[1]}{[2]} + p^2 x^2 \lambda^2 \frac{[1][3]}{[2][4]} + \dots \right\} \\ &\quad \left\{ 1 + p x \lambda^{-1} \frac{[1]}{[2]} + p^2 x^2 \lambda^{-2} \frac{[1][3]}{[2][4]} + \dots \right\}\end{aligned}$$

The coefficient of x^n in the product of these two series is

$$\begin{aligned}p^n \left\{ \frac{[1] \dots [2n-1]}{[2] \dots [2n]} e^{2ni\theta} + \frac{[1] \dots [2n-3]}{[2] \dots [2n-2]} \frac{[1]}{[2]} e^{2(n-2)i\theta} \right. \\ \left. + \dots + \frac{[1] \dots [2n-1]}{[2] \dots [2n]} e^{-2ni\theta} \right\}. \quad (20) \\ = p^n \frac{[2n]!}{\{[2][4] \dots [2n]\}^2} \left\{ 2 \cos 2n\theta + \frac{[2n]}{[2][2n-1]} 2 \cos 2(n-2)\theta \right. \\ \left. + \frac{[3]}{[2][4]} \cdot \frac{[2n][2n-2]}{[2n-1][2n-3]} 2 \cos 2(n-4)\theta + \dots \right\} \\ = p^n \frac{[2n]!}{\{[2][4] \dots [2n]\}^2} (\cos 2\theta).\end{aligned}$$

In case $p = 1$, this coefficient is a well-known form of Legendre's coefficient $P_n \cos 2\theta$.

* ' Lond. Math. Socy. Proc., series 2, vol. 2, p. 193.

$$(1 - 2p^2x \cos 2\theta + p^4x^2)_{-1} = 1 + xp^2\mathfrak{P}_1(\cos 2\theta) + x^2p^4\mathfrak{P}_2(\cos 2\theta) + \dots \quad (21)$$

Making $x = 1$, we obtain at once from this a series for Jacobi's function sn , viz. :—

$$\frac{k^{\frac{1}{2}}}{2q^{\frac{1}{2}}} \frac{sn(2K\theta/\pi)}{\sin \theta} = 1 + q^2\mathfrak{P}_1(\cos 2\theta) + q^4\mathfrak{P}_2(\cos 2\theta) + \dots, \quad (22)$$

because
$$(1 - 2p^2 \cos 2\theta + p^4)_{-1} = \prod_{n=1}^{\infty} \frac{(1 - 2p^{2n} \cos 2\theta + p^{4n})}{(1 - 2p^{2n-1} \cos 2\theta + p^{4n-2})}.$$

It follows that

$$\frac{k^{\frac{1}{2}}K}{\pi q^{\frac{1}{2}}} = 1 + q^2\mathfrak{P}_1(1) + q^4\mathfrak{P}_2(1) + \dots + q^{2n}\mathfrak{P}_n(1) + \dots \quad (23)$$

in which

$$\mathfrak{P}_n(1) = p^n \frac{[2n]!}{\{[2] \dots [2n]\}^2} \left\{ 1 + \frac{[2n]}{[2][2n-1]} + \frac{[3]}{[2][4]} \cdot \frac{[2n][2n-2]}{[2n-1][2n-3]} + \dots + 1 \right\}.$$

In precisely the same way we see that

$$\begin{aligned} (1 - p^s \lambda x)_{-1} &= \mathbf{L}_{x=\infty} \frac{(1 - p^s \lambda x)(1 - p^4 \lambda x) \dots (1 - p^{2n+2} \lambda x)}{(1 - p^{s-2} \lambda x)(1 - p^{4-s} \lambda x) \dots (1 - p^{2n+2-s} \lambda x)}, \\ &= 1 + p^{s-2} \frac{[s]}{[2]} x \lambda + p^{4-2s} \frac{[s][s+2]}{[2][4]} x^2 \lambda^2 + \dots + p^{n(2-s)} \frac{[s] \dots [s+2n-2]}{[2][4] \dots [2n]} x^n \lambda^n + \dots, \end{aligned}$$

and by taking the product of two such series, viz., $(1 - p^s \lambda x)_{-1} (1 - p^s \lambda^{-1} x)_{-1}$, we find

$$\prod_{n=1}^{\infty} \frac{(1 - 2xp^{2n} \cos 2\theta + x^2 p^{4n})}{(1 - 2xp^{2n-s} \cos 2\theta + x^2 p^{4n-2s})} = 1 + \sum x^n p^{2n-s} \mathfrak{P}_n'(\cos 2\theta). \quad (24)$$

$$\mathfrak{P}_n'(\cos 2\theta) = \left\{ \frac{[s][s+2] \dots [s+2n-2]}{[2][4] \dots [2n]} 2 \cos 2n\theta + \frac{[s][s+2] \dots [s+2n-4]}{[2][4] \dots [2n-2]} \cdot \frac{[s]}{[2]} 2 \cos 2(n-2)\theta + \dots \right\} \quad (25)$$

In case s be an odd integer, the infinite product may be written

$$\prod_{r=1}^{r=(s-1)/2} \frac{1}{(1 - 2xp^{2r-s} \cos 2\theta + x^2 p^{4r-2s})} \cdot \prod_{n=1}^{\infty} \frac{(1 - 2xp^{2n} \cos 2\theta + x^2 p^{4n})}{(1 - 2xp^{2n-1} \cos 2\theta + x^2 p^{4n-2})}.$$

The expansion in powers of x of the first of these products is well known—

$$\begin{aligned} &1 + c_1 x + c_2 x^2 + \dots \\ c_n &= p^{n(2-s)} \frac{[s-1][s+1][s+3] \dots [s+2n-3]}{[2][4] \dots [2n]} \\ &\quad \left\{ 2 \cos 2n\theta + \frac{[2n][s-1]}{[2][s+2n-3]} 2 \cos 2(n-2)\theta + \dots \right\}; \end{aligned}$$

hence the following relation will hold among the coefficients $\mathfrak{P}_n, \mathfrak{P}_n', c$:—

$$\mathfrak{P}_n' = \mathfrak{P}_n + c_1 \mathfrak{P}_{n-1} + c_2 \mathfrak{P}_{n-2} + \dots + c_n. \quad (26)$$

Series involving q Forms of Bessel's Coefficients.

In this section certain series expressions for elliptic functions will be found which will contain coefficients denoted $I_{[n]}, J_{[n]}$, etc.

$$I_{[n]}(a) = \sum_{r=0}^{\infty} \frac{a^{n+2r}}{\{2n+2r\}! \{2r\}!} = i^{-n} J_{[n]}(ia), \quad (27)$$

$J_{[n]}$ being the generalised Bessel function.* If we invert the base p in the function $I_{[n]}$, that is, replace p by p^{-1} , we obtain

$$p^{n^2} \sum_{r=0}^{\infty} \frac{a^{n+2r}}{\{2n+2r\}! \{2r\}!} p^{2r(n+r)},$$

which we denote

$$p^{n^2} I_{[n]}(a).$$

Similarly, by inversion of the base p in the function $J_{[n]}$, we obtain

$$\begin{aligned} p^{n^2} \sum_{r=0}^{\infty} (-1)^r \frac{a^{n+2r}}{\{2n+2r\}! \{2r\}!} p^{2r(n+r)}, \\ = p^{n^2} \mathfrak{J}_{[n]}(a), \end{aligned} \quad (29)$$

and not $p^n \mathfrak{J}_{[n]}(a/p)$, as is erroneously stated.†

From the well-known equation

$$\prod_{m=1}^{\infty} \{1 + p^m x\} = 1 + \frac{px}{(p-1)} + \frac{p^2 x^2}{(p-1)(p^2-1)} + \dots,$$

we deduce that

$$\prod_1^{\infty} \{1 + \lambda(p-1)p^{-m}\} = 1 + \frac{\lambda}{[1]} + \frac{\lambda^2}{[2]} + \dots = E_p(\lambda). \quad (p > 1). \quad (30)$$

$$\begin{aligned} \prod_{m=0}^{\infty} \{1 + \lambda(1-p)p^m\} &= 1 + \frac{\lambda}{[1]} + p \frac{\lambda^2}{[2]} + \dots + p^{r(r-1)/2} \frac{\lambda^r}{[r]} + \dots, \\ &= E_p(\lambda). \end{aligned} \quad (p < 1)$$

If we change the base p into p^2 , and write $xt/p+1$ for λ , we find

$$\prod_{m=1}^{\infty} \left\{ 1 + \frac{xt(p^2-1)}{p+1} p^{-2m} \right\} = 1 + \frac{xt}{[2]} + \frac{x^2 t^2}{[2][4]} + \dots,$$

and, as in the case of Bessel's coefficients,

$$\exp \left\{ \frac{x}{2} (t + t^{-1}) \right\} = I_0(x) + \sum_{n=1}^{\infty} (t^n + t^{-n}) I_n(x),$$

* 'Roy. Soc. Proc.,' vol. 74, p. 67.

† *Ibid.*

so

$$\prod_{n=1}^{\infty} \{(1+xt(p-1)p^{-2n})(1+xt^{-1}(p-1)p^{-2n})\} = E_p\left(\frac{xt}{[2]}\right) \times E_p\left(\frac{xt^{-1}}{[2]}\right) \\ = I_{[0]}(x) + \sum (t^n + t^{-n}) I_{[n]}(x), \quad (31)$$

and by a change of the variable x , on replacing t by $e^{2i\theta}$, we find

$$\prod_{n=1}^{\infty} \{1 - 2xp^{-2n} \cos 2\theta + x^2 p^{-4n}\} = I_{[0]}\left(\frac{x}{1-p}\right) + \sum_1 (t^n + t^{-n}) \cdot I_{[n]}\left(\frac{x}{1-p}\right). \quad (32)$$

The convergence of the infinite product requires $p > 1$. Replace p by q^{-1} , x by ix .

$$\prod_{n=1}^{\infty} \{1 - 2xq^{2n} \cos 2\theta + x^2 q^{4n}\} = \mathfrak{J}_{[0]}\left(\frac{qix}{q-1}\right) + \sum_{n=1}^{\infty} 2q^{n^2} i^{-n} \cos 2n\theta \cdot \mathfrak{J}_{[n]}\left(\frac{qix}{q-1}\right), \\ (q < 1). \quad (33)$$

In the notation of Tannery and Molk,* this may be written

$$\frac{\mathfrak{J}_1(\nu)}{2q_0 q^{\frac{1}{2}} \sin \nu\pi} = \mathfrak{J}_{[0]}\left(\frac{qi}{q-i}\right) + 2 \sum_{n=1}^{\infty} q^{n^2} i^{-n} \cos 2n\nu\pi \mathfrak{J}_{[n]}\left(\frac{qi}{q-i}\right), \quad (34)$$

or in terms of Jacobi's functions,

$$\frac{H(2Kx/\pi)}{2q_0 q^{\frac{1}{2}} \sin x} = \mathfrak{J}_{[0]}\left(\frac{qi}{q-1}\right) + 2 \sum_1 q^{n^2} i^{-n} \cos 2nx \cdot \mathfrak{J}_{[n]}\left(\frac{qi}{q-1}\right). \quad (35)$$

The functions denoted $\mathfrak{J}_2(\nu)$, $\mathfrak{J}_3(\nu)$, $\mathfrak{J}_4(\nu)$ by Tannery and Molk may be similarly expressed as

$$\left. \begin{aligned} \frac{\mathfrak{J}_2(\nu)}{2q_0 q^{\frac{1}{2}} \cos \nu\pi} &= \mathfrak{J}_{[0]}\left(\frac{iq}{1-q}\right) + 2 \sum q^{n^2} i^{-n} \cos 2\nu\pi \cdot \mathfrak{J}_{[n]}\left(\frac{iq}{1-q}\right), \\ \frac{\mathfrak{J}_3(\nu)}{q_0} &= \mathfrak{J}_{[0]}\left(\frac{i}{1-q}\right) + 2 \sum q^{n^2} i^{-n} \cos 2\nu\pi \cdot \mathfrak{J}_{[n]}\left(\frac{i}{1-q}\right), \\ \frac{\mathfrak{J}_4(\nu)}{q_0} &= \mathfrak{J}_{[0]}\left(\frac{i}{q-1}\right) + 2 \sum q^{n^2} i^{-n} \cos 2\nu\pi \cdot \mathfrak{J}_{[n]}\left(\frac{i}{q-1}\right). \end{aligned} \right\} \quad (36)$$

A more general series than the foregoing, but of similar type, may be obtained from the expression

$$E_p\left(\frac{xt}{[2]}\right) \times E_p\left(\frac{p^{2\nu} xt^{-1}}{[2]}\right) = \sum_{n=-\infty}^{+\infty} p^{n(n-\nu)} I_{[n]}(xp^{\nu-1}) t^n,$$

from which we deduce

$$\prod_{n=0}^{\infty} \{(1+p^{2n}xt)(1+p^{2n+2\nu}xt^{-1})\} = \sum_{n=-\infty}^{+\infty} p^{n(n-\nu)} I_{[n]}\left(\frac{p^{\nu-1}x}{1-p}\right) t^n. \quad (37)$$

* 'Fonctions Elliptiques,' vol. 2, p. 18.

Replacing t by $e^{i\theta}$, p by $e^{i\nu}$, we find that if ν be a positive integer,

$$\prod_{m=0}^{\nu-1} (1 + p^{2m} x e^{i\theta}) \prod_{m=\nu}^{\infty} \{1 + 2xp^{2m} \cos \theta + x^2 p^{4m}\} \\ = I_{[0]} \left(\frac{p^{\nu-1} x}{1-p} \right) + 2 \sum_1^{\infty} p^{n^2} \cos n(\theta - \nu\omega) I_{[n]} \left(\frac{p^{\nu-1} x}{1-p} \right). \quad (38)$$

In case $\nu=1$ we find on replacing x by $p^2 x$ that the theorem is in agreement with (33). A great number of interesting relations may be found among the various coefficients in the expansion of the products of the form $\prod (1 + 2p^{2m} x \cos \theta + p^{4m} x^2)$, but the investigation of these would not be in line with the rest of this paper.

4.

$$G_p(x, \omega).$$

This function is the simplest function satisfying a difference equation

$$f(x + \omega) = \Gamma_p(x, \omega) f(x), \quad (39)$$

and in p function theory the analogue of the G function of Alexiewsky, which satisfies the difference equation

$$f(x+1) = \Gamma(x) f(x).$$

A history of this function is given by E. W. Barnes in the 'Quarterly Journal of Mathematics,' vol. 31, p. 264, *et seq.* In case $|p^\omega| > 1$, the expression defining $G_p(x, \omega)$ is

$$G_p(x + \omega, \omega) = L \frac{\Gamma_p(\omega) \Gamma_p(2\omega) \dots \Gamma_p(\kappa\omega)}{\Gamma_p(x + \omega) \Gamma_p(x + 2\omega) \dots \Gamma_p(x + \kappa\omega)} \{ \Gamma_p(\kappa\omega + \omega) \}^{x/\omega} \\ [\kappa\omega + \omega]^{x(x-\omega)/2\omega^2} p^{x(x-\omega)(x-2\omega)/6\omega^2}, \quad (40)$$

in which Γ_p is the function defined in (1, α). In case $|p^\omega| < 1$, the proper expression for the function satisfying the difference equation (39) is

$$G_p(x + \omega, \omega) = L \frac{\Gamma_p(\omega) \Gamma_p(2\omega) \dots \Gamma_p(\kappa\omega)}{\Gamma_p(x + \omega) \Gamma_p(x + 2\omega) \dots \Gamma_p(x + \kappa\omega)} \{ \Gamma_p(\kappa\omega + \omega) \}^{x/\omega} \\ [\kappa\omega + \omega]^{x(x-\omega)/2\omega^2}, \quad (41)$$

in which Γ_p is the function defined by the expressions (1) and (B), viz., the expressions for the simplest function satisfying $f(x + \omega) = [x]f(x)$ in case $|p^\omega| < 1$.

As in 'Proc. R. S.,' vol. 74, p. 72, it may be shown that

$$G_p(x + \omega, \omega) = \Gamma_p(x, \omega) G_p(x, \omega), \quad (42)$$

we proceed to investigate a quasi-multiplication theorem for this function, and thence to deduce a transformation theorem for a function which satisfies a difference equation

$$f(x) = \sigma(x) f(x - \omega).$$

Multiplication Theorem.

The theorem to be discussed is a generalisation of a theorem given by E. W. Barnes,* viz. :—

$$\prod_{r=0}^{n-1} \prod_{s=0}^{n-1} G\left(x + \frac{r+s}{n}\right) = K (2\pi)^n (n-1)! n^{-n^2/2 + nx} G(nx).$$

We have shown that

$$\Gamma_p^1(nx, \omega) = A \left[\frac{1}{n}\right]^{-nx/\omega} \Gamma_p\left(x + \frac{\omega}{n}\right) \dots \Gamma_p\left(x + \frac{n-1}{n} \omega\right),$$

in which

$$A = \frac{\left[\frac{1}{n}\right]}{\prod_{r=0}^{n-1} \left\{ \Gamma_p\left(\frac{r\omega}{n}\right) \right\}}.$$

$$\text{Consider } f(x) = \frac{A^{nx/\omega} \left[\frac{1}{n}\right]^{-nx(nx-\omega)/2\omega^2} \prod_{r=0}^{n-1} \prod_{s=0}^{n-1} G_p\left(x + \frac{r+s}{n} \omega\right)}{G_p^1(nx, \omega)}.$$

Now

$$\begin{aligned} G_p^1(nx + n\omega, \omega) &= \Gamma_p^1(nx) \Gamma_p^1(nx + \omega) \dots \Gamma_p^1(nx + \overline{n-1}\omega) G_p^1(nx, \omega), \\ &= \prod_{r=0}^{n-1} \left\{ A \left[\frac{1}{n}\right]^{-\frac{n}{\omega} \left(x + \frac{r\omega}{n}\right)} \Gamma_p\left(x + \frac{r\omega}{n}\right) \dots \Gamma_p\left(x + \frac{r+n-1}{n} \omega\right) \right\} \times G_p^1(nx, \omega), \\ &= A^n \left[\frac{1}{n}\right]^{-n^2x/\omega - n(n-1)/2} \prod_{r=0}^{n-1} \prod_{s=0}^{n-1} \left\{ \Gamma_p\left(x + \frac{r+s}{n} \omega\right) \right\} \cdot G_p^1(nx), \end{aligned}$$

therefore

$$\frac{f(x+\omega)}{f(x)} = A^{n(x+\omega)/\omega - nx/\omega - n} \left[\frac{1}{n}\right]^{-(nx+n\omega)(nx+n\omega-\omega)/2\omega^2 + nx(nx-\omega)/2\omega^2 + n^2x/\omega + n(n-1)/2} = 1.$$

The function $f(x)$ has no singularities in the positive part of the x plane, it is also a single-valued function, since by p^x we always denote absolute values.

By Lionville's theorem $f(x)$ is constant, and we may write its value as

• $f\left(\frac{\omega}{n}\right)$. Finally

$$G_p^1(nx, \omega) = \lambda C^n \left[\frac{1}{n}\right]^{-nx(nx-\omega)/2\omega^2} \prod_{r=0}^{n-1} \prod_{s=0}^{n-1} G_p\left(x + \frac{r+s}{n} \omega, \omega\right), \quad (43)$$

in which

$$\lambda = \frac{\prod_{r=0}^{n-1} \left\{ \Gamma_p\left(\frac{r\omega}{n}\right) \right\}}{\prod_{r=0}^{n-1} \prod_{s=0}^{n-1} \left\{ G_p\left(\frac{r+s+1}{n} \omega\right) \right\}} \left[\frac{1}{n}\right]^{-1}, \text{ and } C = A^{n/\omega} = \left[\frac{1}{n}\right]^{n/\omega} \left\{ \prod_{r=0}^{n-1} \left(\Gamma_p\left(\frac{r\omega}{n}\right) \right) \right\}^{-n/\omega}$$

* 'Q. J. M.', 1899, p. 291.

This theorem is consistent in form with the multiplication theorem of the G function, and reduces to Barnes' expression if we make $p = 1$, $\omega = 1$.

5.

$$T_p(x, \omega).$$

By means of the function $G_p(x, \omega)$ we can form a function satisfying a difference equation

$$f(x) = \sigma(x) f(x - \omega).$$

$$\text{Take} \quad T_p(x) = \frac{G_p(\omega + x)}{G_p(\omega - x)}, \quad (44)$$

$$\text{then} \quad T_p(x - \omega) = \frac{G_p(x)}{G_p(2\omega - x)}.$$

Combining these with $G_p(x + \omega) = \Gamma_p(x, \omega) G_p(x)$, we find that

$$T_p(x - \omega) = \Gamma_p(x) \Gamma_p(\omega - x) T_p(x),$$

$$\text{which is} \quad T_p(x) = \lambda^{-1} S_p(x) T_p(x - \omega). \quad \lambda^{\frac{1}{2}} = \Gamma_p\left(\frac{\omega}{2}, \omega\right). \quad (45)$$

Now $S_p(x)$ may be expressed as $Ae^{ax+bx^2}\sigma(x) = S_{q^2}\left(\frac{x}{2\omega_2}, 1\right)$, (Result (16)) in which

$$\begin{aligned} A &= \frac{\pi}{\omega_1} (q^2 - 1)^{-1} \{\Gamma_{q^2}(\tfrac{1}{2})\}^2 e^{\frac{i\pi}{2}}, & b &= -\frac{\eta_1}{2\omega_1}, \\ a &= \frac{i\pi}{2\omega_1}, & q &= e^{\frac{i\pi\omega_2}{\omega_1}}, \end{aligned}$$

so that on writing

$$f(x) = e^{ax+\beta x^2+\gamma x^3} \Gamma_{q^2}\left(\frac{x}{2\omega_2}\right), \quad (46)$$

we can determine the constants a, β, γ , that

$$f(x) = \sigma(x) f(x - 2\omega_2),$$

$$\text{for} \quad \frac{f(x)}{f(x - 2\omega_2)} = e^{ax+\beta x^2+\gamma x^3 - a(x-2\omega_2) - \beta(x-2\omega_2)^2 - \gamma(x-2\omega_2)^3} \lambda^{-1} A e^{ax+bx^2} \sigma(x).$$

Choosing

$$\left. \begin{aligned} 6\gamma\omega_2 + b &= 0, & \text{we find} \quad \gamma &= -\frac{\eta_1}{12\omega_1\omega_2}, \\ 4\beta\omega_2 - 12\gamma\omega_2^2 + a &= 0, & \beta &= -\frac{i\pi}{8\omega_1\omega_2} - \frac{\eta_1}{4\omega_1}, \\ 2a\omega_2 - 4\beta\omega_2^2 + 8\gamma\omega_2^3 - \log \lambda &= 0, & a &= -\frac{\omega_2\eta_1}{6\omega_1} - \frac{i\pi}{4\omega_1} + \frac{i\pi}{4\omega_2} + \frac{1}{2\omega_2}, \\ & & \log(q^2 - 1) - \frac{1}{2\omega_2} \log \frac{\pi}{\omega_1} & \end{aligned} \right\} \quad (47)$$

$$\begin{aligned}
 f(x) &= \sigma(x) f(x-2\omega_2), \\
 f(x-2\omega_2) &= \sigma(x-2\omega_2) f(x-4\omega_2), \\
 &\vdots \qquad \qquad \qquad \vdots \\
 f(x-2n-2\omega_2) &= \sigma(x-2n-2\omega_2) f(x-2n\omega_2), \\
 f(x) &= \sigma(x) \sigma(x-2\omega_2) \dots \sigma(x-2n-2\omega_2) f(x-2n\omega_2),
 \end{aligned} \tag{48}$$

and since

$$\sigma(x-2m\omega_2) = (-1)^m e^{2\pi i m (mx - m^2 \omega_2)},$$

we obtain

$$f(x) = \{\sigma(x)\}^n (-1)^{\frac{n(n-1)}{2}} e^{2\pi i \frac{n(n-1)}{2} x - \pi i \frac{(n-1)n(2n-1)}{3} \omega_2} \times f(x-2n\omega_2). \tag{49}$$

In connection with this function, we notice that Picard has given a function, $F(z)$, such that

$$F(z+2\omega_1) = F(z), \qquad F(z+2\omega_2) = e^{n\pi iz/\omega_1} S(z) F(z),$$

in which $S(z)$ is a given doubly periodic function of the first kind.*

Transformation Theorem for the Function $T_p(x, \omega)$.

By means of the quasi-multiplication theorem of the G_p function,

$$G_{p_2}^1(n\omega, \omega) = \lambda C^x \left[\frac{1}{n} \right]^{-n, x(n\omega - \omega)/2\omega^2} \prod_{r=0}^{n-1} \prod_{s=0}^{n-1} G_p \left(x + \frac{r+s}{n} \omega \right),$$

we derive

$$\begin{aligned}
 T_{p_2}^1(n\omega) &= G_{p_2}^1(\omega + n\omega, \omega) / G_{p_2}^1(\omega - n\omega, \omega) \\
 &= C^{2x} \left[\frac{1}{n} \right]^{-n^2 x^2 / \omega^2} \prod_0^{n-1} \prod_0^{n-1} \left\{ G_p \left(x + \frac{r+s+1}{n} \omega \right) / G_p \left(x + \frac{r+s-1}{n} \omega \right) \right\}. \tag{50}
 \end{aligned}$$

* Cf. Forsyth, 'Theory of Functions, p. 296, Ex. 3.

Writing the double product of the quotient of the G functions as

$$\begin{array}{l}
 \left. \begin{array}{l}
 G\left(x + \frac{\omega}{n}\right) G\left(x + \frac{2\omega}{n}\right) \dots G\left(x + \frac{n\omega}{n}\right) \\
 \times G\left(x + \frac{2\omega}{n}\right) G\left(x + \frac{3\omega}{n}\right) \dots G\left(x + \frac{n-1}{n}\omega\right) \\
 \dots \dots \dots \\
 \times G\left(x + \frac{n-1}{n}\omega\right) \dots \dots \dots G\left(x + \frac{2n-2}{n}\omega\right) \\
 \times G\left(x + \frac{n\omega}{n}\right) \dots \dots \dots G\left(x + \frac{2n-1}{n}\omega\right)
 \end{array} \right\} \quad (51) \\
 \hline
 \begin{array}{l}
 G\left(\omega - x - \frac{n-1}{n}\omega\right) G\left(\omega - x - \frac{n-2}{n}\omega\right) \dots G(\omega - x) \\
 \times G\left(\omega - x - \frac{n-2}{n}\omega\right) G\left(\omega - x - \frac{n-3}{n}\omega\right) \dots G\left(\omega - x + \frac{\omega}{n}\right) \\
 \dots \dots \dots \\
 \times G(\omega - x) G\left(\omega - x + \frac{\omega}{n}\right) \dots \dots \dots G\left(\omega - x + \frac{n-1}{n}\omega\right)
 \end{array}
 \end{array}$$

we take the last term of the first row in the numerator with the first term of the last row in the denominator, the last but one of the first row with the second of the last row. In the same way we collect the terms of the second row of the numerator and the last row but one of the denominator, and so on, and finally obtain the expression

$$\left. \begin{array}{l}
 T(x) T\left(x - \frac{\omega}{n}\right) \dots T\left(x - \frac{n-1}{n}\omega\right) \\
 \times T\left(x + \frac{\omega}{n}\right) T(x) \dots T\left(x - \frac{n-2}{n}\omega\right) \\
 \dots \dots \dots \\
 \times T\left(x + \frac{n-1}{n}\omega\right) \dots \dots T(x)
 \end{array} \right\} \quad (52)$$

so that
$$T_{p_1}(nx, \omega) = C^{2x} \left[\frac{1}{n} \right]^{-\frac{n^2 x^2}{\omega^2} \prod_{r=0}^{n-1} \prod_{s=0}^{-(n-1)} T_p\left(x + \frac{r+s}{n}\omega, \omega\right)}. \quad (53)$$

This theorem is the extension of the theorems

$$\begin{aligned}
 S_p\left(x, \frac{\omega}{n}\right) &= CS_p(x, \omega) S_p\left(x + \frac{\omega}{n}, \omega\right) \dots S_p\left(x + \frac{n-1}{n}\omega, \omega\right), \\
 \sin(nx) &= c \sin x \sin\left(x + \frac{\pi}{n}\right) \dots \sin\left(x + \frac{n-1}{n}\pi\right).
 \end{aligned}$$

6.

$$G_p(x, \omega_1, \omega_2).$$

Consider the doubly infinite product

$$G_p(x, \omega_1, \omega_2) = [x] \prod_{m=0}^{\infty} \prod_{n=0}^{\infty} \frac{[x + m\omega_1 + n\omega_2]}{[m\omega_1 + n\omega_2]}, \quad (54)$$

simultaneous zero values of m and n being excluded from the product.

This product is absolutely convergent if $|p^{\omega}| < 1$.

By means of the expression

$$\Gamma_p(x, \omega) = \frac{1}{[x]} \prod_{n=1}^{\infty} \frac{[m\omega]}{[x + m\omega]} [\kappa\omega]^{x/\omega} = (1-p)^{-x/\omega} \frac{1}{[x]} \prod_{n=1}^{\infty} \frac{[m\omega]}{[x + m\omega]} \quad (|p^{\omega}| < 1)$$

we are enabled to write the double product as

$$\begin{aligned} & [x] \prod_{n=1}^{\infty} \frac{[x + m\omega_1]}{[m\omega_1]} \prod_{n=1}^{\infty} \prod_{m=1}^{\infty} \frac{[x + m\omega_1 + n\omega_2]/[n\omega_2]}{[m\omega_1 + n\omega_2]/[n\omega_2]} \\ &= (1-p)^{-x/\omega_1} \Gamma_p^{-1}(x, \omega_1) \prod_{m=0}^{\infty} \frac{[x + m\omega_1]^{-1} (1-p)^{-(x+m\omega_1)/\omega_2} \Gamma_p^{-1}(x + m\omega_1, \omega_2)}{[m\omega_1]^{-1} (1-p)^{-m\omega_1/\omega_2} \Gamma_p^{-1}(m\omega_1, \omega_2)} \\ &= (1-p)^{-x/\omega_1} \Gamma_p^{-1}(x, \omega_1) \prod_{m=0}^{\infty} \left\{ \frac{\Gamma_p(m\omega_1 + \omega_2, \omega_2)}{\Gamma_p(x + m\omega_1 + \omega_2, \omega_2)} (1-p)^{-x/\omega_2} \right\} \dots \\ &= (1-p)^{-x/\omega_1} \Gamma_p^{-1}(x, \omega_1) \frac{\Gamma_p(\omega_2, \omega_2)}{\Gamma_p(x + \omega_2, \omega_2)} \times \prod_{m=1}^{\infty} \left\{ \frac{\Gamma_p(m\omega_1 + \omega_2, \omega_2)}{\Gamma_p(x + m\omega_1 + \omega_2, \omega_2)} (1-p)^{-x/\omega_2} \right\} \\ &= (1-p)^{-x/\omega_1} \Gamma_p^{-1}(x, \omega_1) \frac{\Gamma_p(\omega_2, \omega_2)}{\Gamma_p(x + \omega_2, \omega_2)} \prod_{n=1}^{\infty} \frac{[m\omega_1]}{[x + m\omega_1]} \\ & \quad \prod_{n=1}^{\infty} \left\{ \frac{\Gamma_p(m\omega_1, \omega_2)}{\Gamma_p(x + m\omega_1, \omega_2)} (1-p)^{-x/\omega_2} \right\} \\ &= (1-p)^{-x/\omega_1} \Gamma_p^{-1}(x, \omega_1) \Gamma_p^{-1}(x + \omega_2, \omega_2) \Gamma_p(x + \omega_1, \omega_1) (1-p)^{x/\omega_1} \\ & \quad \prod_{m=1}^{\infty} \left\{ \frac{\Gamma_p(m\omega_1, \omega_2)}{\Gamma_p(x + m\omega_1, \omega_2)} (1-p)^{-x/\omega_2} \right\} \\ &= \frac{[x]}{\Gamma_p(x + \omega_2, \omega_2)} \prod_{n=1}^{\infty} \left\{ \frac{\Gamma_p(m\omega_1, \omega_2)}{\Gamma_p(x + m\omega_1, \omega_2)} (1-p)^{-x/\omega_2} \right\}, \end{aligned}$$

so that finally we have

$$G_p(x, \omega_1, \omega_2) \Gamma_p(x, \omega_2) = \prod_{m=1}^{\infty} \left\{ \frac{\Gamma_p(m\omega_1, \omega_2)}{\Gamma_p(x + m\omega_1, \omega_2)} (1-p)^{-x/\omega_2} \right\}, \quad (55)$$

and a similar equation obtained by transposing ω_1, ω_2 . The transformation carried out in the above work is on the same lines as a transformation given by E. W. Barnes for a function $G(x|\tau)$,* but is simpler owing to the fact that the products are convergent in the above case without necessity arising for the introduction of exponential factors to secure convergence.

* 'Lond. Math. Socy. Proc.', vol. 31, p. 360.

There are two difference equations for the function

$$\left. \begin{aligned} G_p(x + \omega_1, \omega_1 \omega_2) &= G_p(x, \omega_1 \omega_2) \Gamma_p(x, \omega_2) \times \frac{(1-p)^{x/\omega_2}}{\lambda_2}, \\ G_p(x + \omega_2, \omega_1 \omega_2) &= G_p(x, \omega_1 \omega_2) \Gamma_p(x, \omega_1) \times \frac{(1-p)^{x/\omega_1}}{\lambda_1}, \end{aligned} \right\} \quad (56)$$

in which $\lambda_1 = \prod_1^{\infty} (1 - p^{n\omega_1}), \quad \lambda_2 = \prod_1^{\infty} (1 - p^{n\omega_2}).$

Since

$$\begin{aligned} \Gamma_p(-x, -\omega) &= \frac{1}{[-x]} \prod_{\kappa=\infty}^1 \frac{[-\omega][-\kappa\omega]}{[-x-\omega][-\kappa\omega]} \frac{[-2\omega] \dots [-\kappa\omega]}{[-x-2\omega] \dots [-x-\kappa\omega]} [-\kappa\omega]^{x/\omega} \\ &= -\frac{p^x}{[x]} \prod_{\kappa=\infty}^1 \frac{[\omega][\kappa\omega]}{[x+\omega][\kappa\omega]} p^{-\frac{x}{2}(\omega+\kappa\omega) + \frac{x}{2}(2x+\omega+\kappa\omega)} p^{-\kappa x} \left(\frac{1-p^{\kappa\omega}}{p-1} \right)^{x/\omega} \\ &= -p^x (-1)^{x/\omega} \Gamma_p(x, \omega) = -p^x e^{2\pi i x/\omega} \Gamma_p(x, \omega). \end{aligned} \quad (57)$$

If now we form a function $\tau(x|\omega_1, \omega_2) = G(x + \omega_1, \omega_1 \omega_2) G(-x, \omega_1, -\omega_2)$, we see that

$$\frac{\tau(x|\omega_1, \omega_2)}{\tau(x + \omega_1|\omega_1, \omega_2)} = \frac{G_p(x + \omega_1, \omega_1 \omega_2) G_p(-x, \omega_1, -\omega_2)}{G_p(x + 2\omega_1, \omega_1, \omega_2) G_p(-x - \omega_1, \omega_1, -\omega_2)}, \quad (58)$$

and by means of the difference equation

$$G_p(x + \omega_1, \omega_1 \omega_2) = G_p(x, \omega_1 \omega_2) \Gamma_p(x, \omega_2) \times \frac{(1-p)^{x/\omega_2}}{\lambda_2}, \quad (59)$$

we are able to reduce the right side of Equation (58) to

$$\frac{\Gamma_p(-x - \omega_1, -\omega_2)}{\Gamma_p(x + \omega_1, \omega_2)} \times \frac{(1-p)^{(-x - \omega_1)/-\omega_2}}{(1-p)^{(x + \omega_1)/\omega_2}} = -p^{x + \omega_1} e^{2i\pi(x + \omega_1)/\omega_2}. \quad (60)$$

Consider now

$$\frac{\tau(x|\omega_1, \omega_2)}{\tau(x + \omega_2|\omega_1, \omega_2)} = \frac{G_p(x + \omega_1, \omega_1 \omega_2) G_p(-x, \omega_1, -\omega_2)}{G_p(x + \omega_1 + \omega_2, \omega_1 \omega_2) G_p(-x - \omega_2, \omega_1, -\omega_2)}.$$

We know that

$$G(-x - \omega_2, \omega_1, -\omega_2) = \Gamma_p(-x, \omega_1) G(-x, \omega_1, -\omega_2) \times \frac{(1-p)^{-x/\omega_1}}{\lambda_1},$$

$$G(x + \omega_1 + \omega_2, \omega_1 \omega_2) = \Gamma_p(x + \omega_1, \omega_1) G(x + \omega_1, \omega_1 \omega_2) \times \frac{(1-p)^{x + \omega_1/\omega_1}}{\lambda_1},$$

therefore

$$\frac{\tau(x|\omega_1, \omega_2)}{\tau(x + \omega_2|\omega_1, \omega_2)} = \frac{\lambda_1 (1-p)^{-x + \omega_1/\omega_1}}{\Gamma_p(x + \omega_1, \omega_1)} = \frac{\lambda_1 (1-p)^{x/\omega_1}}{\Gamma_p(-x, \omega_1)} = \frac{\lambda_1^2 (1-p)^{-1} S_p(x + \omega_1, \omega_1)}{\left\{ \Gamma_p\left(\frac{\omega_1}{2}, \omega_1\right) \right\}^2}. \quad (61)$$

It is now quite clear from the difference equations (59) and (60) that we can, by the introduction of an exponential factor, construct the function denoted $F(x)$ by Picard*

* Cf. Forsyth, 'Theory of Functions,' p. 296.

$$F(x+2\omega_1) = F(x),$$

$$F(x+2\omega_2) = e^{n\pi iz/\omega_1} S(x) F(x),$$

$$F(x) = Ae^{\int \left\{ \frac{S'(x)}{S(x)} + \frac{n\pi i}{\omega_1} \right\} \Pi(x) dx},$$

where A is a constant and $\Pi(x)$ denotes

$$\frac{\eta_1 x}{i\pi} + G + \Sigma \left\{ B_r + C_r \frac{d}{dx} + D_r \frac{d^2}{dx^2} + \dots \right\} \zeta(x - b_r),$$

the summation extending over all points b_r and the constants B_r, \dots being subject to the relation

$$\Sigma B_r = -\frac{\omega_1}{2\pi}.$$

Further Researches on the Temperature Classification of Stars. No. 2.

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[PLATE 3.]

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1. *Introduction.*

In a previous paper * discussing the photographs of stellar spectra taken with the calcite prismatic camera, I showed that the variation of the position of maximum intensity, when we dealt with the various genera of stars, corresponded with the temperature change—including in that term the possible results of electrical energy †—suggested by the Chemical Classification.

2. *Object of the Present Research.*

Obviously the next test to apply to the temperature curve based upon the Chemical Classification was to compare, under similar conditions, the relative temperatures of those genera placed on the same temperature horizon but on

* 'Roy. Soc. Proc.,' vol. 73, pp. 227—238, 1904.

† In reference to the possible effects of the variation of electrical conditions, I wish to point out that, whilst employing the general term "temperature variation," I have always made a reservation for the inclusion of possible electrical effects.

I take this opportunity of emphasising this "caveat" because I find that in his 'Handbuch der Spectroscopie,' Professor Kayser states (see vol. 2, p. 275) that I have always only considered temperature effects. His exact words are "spricht Lockyer immer nur von einem Einfluss der Temperatur, über welche wir beim Funken nichts wissen." This is certainly not in accordance with my published statements, for more than 30 years ago, whilst discussing the dissociation effects of increasing "temperature," I especially mentioned (see 'Roy. Soc. Proc.,' vol. 22, p. 372, section 2, June, 1874) that the action of electricity must be included in the term "temperature," and I have, on many occasions, repeated this statement.

the opposite sides of the curve, since the chemical evidence indicated that, while there are differences in the conditions of absorption in such genera, their temperatures are approximately the same.*

3. Order of Procedure.

This second test has now been applied to the Chemical Classification with the results given below.

The peculiar difficulties of a research of this kind were enumerated in the former paper, but they were increased in the present case by the restriction of the number of combinations possible when the selection of suitable pairs of stars for comparison was confined to the same temperature horizon.

The following table shows the number of pairs on each horizon available for comparison, and also the number which has been dealt with in each case.

Table I.

Horizon.	Types.	Number of pairs readily comparable throughout the year.	Number of pairs photographed.
8	Crucian-Achernian	2	1
7	Taurian-Argolian	2	1
6	Rigelian-Markabian	4	1
3	Polarian-Procyonian	9	6
2	Aldebaran-Arcturian	16	4

Although the Argonian (Stage 10) and Alnitamian (Stage 9) groups, from their position at the apex of the curve, offer no comparisons, their spectra should show them to be nearly alike. As there is no Argonian star in the northern hemisphere, with the possible exception of λ Cephei, which Mrs. Fleming has recently found to be identical in its spectrum with ζ Puppis, † but which is too faint to be photographed with the present instrument, this point has not been tested. The Cygnian (Stage 5) and Sirian (Stage 4) groups

* The existence of such a difference in the absorbing conditions was pointed out by me from theoretical considerations in 1887 ('Roy. Soc. Proc.,' vol. 43, p. 146), but Professor E. C. Pickering was the first to demonstrate its actual presence. In the "Spectra of Bright Stars" ('Harvard College Observatory Annals,' vol. 28, Part I, p. 5) he found it necessary when classifying the spectra to divide them into two classes according to the relative widths of the hydrogen and metallic lines.

† "Harvard College Observatory Circulars," No. 92.

have no analogues on the opposite sides of the curve, and cannot, therefore, enter into the present discussion, whilst the Piscian stars (Stage 1, descending) are both too faint to be available with the present camera, and therefore the lowest stage (the Antarian-Piscian) cannot be considered.

Long periods of bad observing weather have greatly hindered the work.

4. *Results.*

A brief description of each of the negatives discussed is given in Table II. It will be remarked from the seventh column that the same make of plates has not been used throughout, but, as each pair of spectra compared are on the same plate, and have, therefore, been subjected to exactly the same treatment in development, etc., this can in no way affect the results. On the publication of the former paper Sir William Abney kindly sent me two plates especially sensitised for the red end of the spectrum, and a number of exposures was made, under test conditions, with several different makes of plates, in order to obtain, if possible, a greater length of spectrum at the red end.

5. *Discussion of Photographs.*

In no case among the present photographs has the variation of the position of greatest intensity in any pair been found so marked as the variations recorded in the previous paper.

A detailed discussion of each negative follows.

Stage 8.

Negative 65 (See No. 1, Plate 3) γ Cassiopeiae (Cruc., ascending)— ϵ Cassiopeiae (Achern., descending). As a result of relatively shorter exposure, the spectrum of ϵ is very slightly weaker throughout. The bright lines in γ are very faint, too faint to show on the enlarged reproduction, but the measurement of their positions on the negative relative to the lines in the ϵ spectrum, shows that on the reproduction (No. 1, Plate 3) they will be 0.25 of an inch nearer the right hand side of the plate.

Notwithstanding a relatively sudden decrease of intensity in the spectrum of ϵ at the more refrangible end of the hydrogen series—whereas the spectrum of γ fades gradually to extinction—both spectra extend to about the same distance into the ultra-violet and their red portions are equally intense.

Note.—There is evidence for assuming that the presence of bright hydrogen in γ Cassiopeiae does not materially affect the absolute extension of the spectrum into the ultra-violet. This point will be dealt with in a subsequent communication.

Table II.

Catalogue number of negative.	Date.	Star.	Type.	Stage. A = ascending. D = descending.	Altitude.	Plate used.	Description.
65	1.10.04	γ Cassiopeie ϵ "	Crucian Achernian	8 A D	68 64	Cadett "Spectrum"	ϵ very slightly weaker throughout with stronger absorption beyond the hydrogen series; no evidence for any difference of temperature. Mixed up with other Pleiades spectra, ζ weaker throughout, but no indications of temperature difference.
71	11.11.04	η Tauri ζ "	Algolian Taurian	7 D A	40 38	"	Exactly similar as regards extension into the red and ultra-violet: both extend far beyond the end of the hydrogen series. Equally exposed: extended equally into both red and ultra-violet.
68	8.10.04	α Andromedæ β Tauri	Markabian Rigelian	6 D A	56 57	"	
60	3.9.04	β Cassiopeie α Persei	Procyonian Polarian	3 D A	77 79	Edwards's "Isochromatic"	
62	9.9.04	β Draconis β Cassiopeie	Polarian Procyonian	3 A D	63 71	"	β Draconis less exposed and, therefore, weaker throughout, but the reduction of intensity is equal at both ends.
64	19.9.04	η Cassiopeie α Persei	Procyonian Polarian	3 D A	76 87	Cadett "Spectrum"	η Cassiopeie fainter throughout the whole spectrum, but extends practically as far into the ultra-violet.
67	3.10.04	γ Cygni β Cassiopeie	Polarian Procyonian	3 A D	71 74	"	Almost identical intensities throughout the entire length of the spectrum.
74	12.1.05	α Persei α Canis Minor	Polarian Procyonian	3 A D	38 32	"	Exposures approximately equal. Red extensions equally intense. Both spectra extend equally far into the ultra-violet, but that of α Persei shows a sudden decrease of intensity at the end of the hydrogen series.
46	21.7.04	γ Draconis "	Aldebarian Arcturian	2 A D	68 67	Edwards's "Isochromatic"	Spectra both faint but of about equal intensity in G to D region, δ , however, extends a little further into the ultra-violet.
72	7.12.04	α Arietis α Tauri	Arcturian Aldebarian	2 D A	57 55	Cadett "Spectrum"	α Tauri slightly stronger in red and blue regions but extends no further into the ultra-violet.

Stage 7.

Negative 71, ζ Tauri (Taur., ascending)— η Tauri (Algol., descending).—The comparison in this case is rendered somewhat difficult owing to the superposition of the spectra of the other Pleiades stars, whilst that of η (Alcyone) was being photographed. Unfortunately the spectrum of ζ is partially covered by that of Maia, and, owing to relative under-exposure, is weaker, than that of η throughout the whole length. Notwithstanding this latter fact, a close examination reveals no inversion of intensity, such as is given by stars of different temperature horizons, in either the red or the ultra-violet ends of the spectra. It may be remarked here that this negative shows the temperature conditions obtaining in each of the Pleiades stars, Atlas—Pleione, Alcyone, Maia and Electro to be about the same.

Stage 6.

Negative 68 (No. 2, Plate 3), α Andromedæ (Mark., descending)— β Tauri (Rig., ascending).—We find both spectra extending equally far into the ultra-violet, and the closest inspection does not bring to light the slightest difference in the red portions.

Stage 3.

Negative 60 (No. 3, Plate 3), β Cassiopeiæ (Proc., descending)— α Persei (Pol., ascending).—The relative exposures on these two stars were equal, and the extensions of the spectra into the ultra-violet show no perceptible difference. A very slight difference does exist, however, between their intensities in the red portions, that of the Polarian star being very slightly the stronger.

Negative 62, β Draconis (Pol., ascending)— β Cassiopeiæ (Proc., descending).—Whilst the spectrum of β Draconis is fainter throughout, the relative intensities of similar radiations in the two spectra vary together, thereby indicating an equality of temperature conditions in the two stars.

Negative 64, η Cassiopeiæ (Proc., descending)— α Persei (Pol., ascending).—In this case the spectra extend equally far into the ultra-violet, although that of η Cassiopeiæ is fainter in the violet, blue, and red regions. The difference is slight but points to a probable, very small, superiority of temperature for the Procyonian star.

Negative 67, γ Cygni (Pol., ascending)— β Cassiopeiæ (Proc., descending).—The two spectra are about equally bright in the H_β — H_γ region, but that of γ Cygni is slightly brighter in the orange-red and does not extend quite so far into the ultra-violet, again showing a slight superiority of temperature for the Procyonian star.

A slight inversion of the spectra of the preceding papers the α lines are uncertain.

Spectra of γ & δ Series. *γ ascending—* and *Alkali γ descending—* The characters of this spectrum are nearly equal and the positions of the lines are the same. Although the spectrum of a γ series shows a slight inversion in intensity at the end of the spectrum where it extends very far out into the ultra-violet as does that of β series. In this spectrum the characters of the two spectra are the same distance from the end of the plate and as may be seen from the relative positions of the H and δ lines, the spectrum of a γ series should be shifted only a small distance to the right thus rendering its absolute extension not the ultra-violet a little more than that of β series.

Group 2.

Spectra of η & θ Series. *η ascending—* and *θ series descending—* Both spectra are similar and as we should expect neither extends very far beyond δ into the ultra-violet. The distances between H_2 and H_3 are approximately equal and the spectrum of η series is slightly stronger in the red and less ultra-violet than is the θ series.

Spectra of ζ & ϕ Series. *ζ series descending—* and *ϕ series ascending—* Very good spectra although rather faint. The bracketed straight section and the portion between H_2 and H_3 in the spectrum of ζ series are slightly stronger than the corresponding parts of the ϕ series spectrum and the latter extends quite as far or even a little farther into the ultra-violet thereby indicating a slightly higher temperature for the ζ series star.

6. General Remarks.

It must be noted that the slight differences existing between some of the parts of spectra discussed are only spectral and are not comparable with the general differences noted in the previous paper. For instance, if we compare the photographs shown in No. 3 Plate 3 of the present paper—and this shows as great a difference as any disclosed during this research—with the first photograph (No. 1 Plate 7 of the previous paper,* we see at once that in the present case there is no indication of the absolute inversion of intensity between the red and ultra-violet ends of the two spectra, such as is shown on the former photograph.

The differences must at the most, be considered as indicating the existence of species within the limits of the genera proposed in the Chemical Classification, and as justifying the "caveat" entered when discussing the terms of that classification.†

* *Ibid.* cit.

† 'B. J. Soc. Proc.' vol. 65, p. 191, 1900.

1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes that proper record-keeping is essential for transparency and accountability, particularly in the context of public administration and financial management.

2. The second part of the document outlines the various methods and tools used to collect and analyze data. It highlights the need for standardized procedures and the use of modern technology to ensure the reliability and validity of the information gathered.

3. The third part of the document focuses on the interpretation and presentation of the data. It discusses the importance of clear communication and the use of visual aids to effectively convey the findings of the study to the relevant stakeholders.

4. The fourth part of the document provides a detailed analysis of the results obtained from the data collection and interpretation process. It identifies key trends, patterns, and areas for improvement, and offers recommendations based on the findings.

5. The fifth part of the document concludes the study by summarizing the main findings and reiterating the importance of ongoing monitoring and evaluation to ensure the continued effectiveness of the implemented measures.

A slight overlap of the spectra on this negative renders the comparison somewhat uncertain.

Negative 74, α Persei (Pol., ascending)— α Canis Minoris (Proc., descending).—The exposures on this negative are nearly equal, and the intensities in the orange-red are the same. Although the spectrum of α Persei shows a sudden decrease in intensity at the end of the hydrogen series, it extends very nearly as far into the ultra-violet as does that of Procyon. On this negative the ultra-violet extremities of the two spectra are the same distance from the end of the plate but, as may be seen from the relative positions of the H and K lines, the spectrum of α Persei should be shifted bodily a small distance to the right, thus rendering its absolute extension into the ultra-violet a little less than that of Procyon.

Stage 2.

Negative 46, γ Draconis (Ald., ascending)— δ Draconis (Arct., descending). Both spectra are faint, and, as we should expect, neither extends very far beyond K into the ultra-violet. The intensities between H_{β} and H_{γ} are approximately equal, but the spectrum of γ Draconis is slightly stronger in the red and does not extend quite so far into the ultra-violet.

Negative 72 (No. 4, Plate 3) α Arietis (Arct., descending)— α Tauri (Ald., ascending). Very good spectra although rather faint. The detached orange-red section and the portion between H_{β} and H_{γ} in the spectrum of Aldebaran are slightly stronger than the corresponding parts of the α Arietis spectrum, but the latter extends quite as far, or even a little farther, into the ultra-violet, thereby indicating a slightly higher temperature for the Arcturian star.

6. *General Remarks.*

It must be noted that the slight differences existing between some of the pairs of spectra discussed are only specific, and are not comparable with the generic differences cited in the previous paper. For instance, if we compare the photograph shown on No. 3, Plate 3 of the present paper—and this shows as great a difference as any disclosed during this research—with the first photograph (No. 1, Plate 7) of the previous paper,* we see at once that in the present case there is no indication of the absolute inversion of intensity between the red and ultra-violet ends of the two spectra, such as is shown on the former photograph.

The differences must, at the most, be considered as indicating the existence of species within the limits of the genera proposed in the Chemical Classification, and as justifying the "caveat" entered when discussing the terms of that classification.†

* *Loc. cit.*

† 'Roy. Soc. Proc.,' vol. 65, p. 191, 1899.

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These photographs also indicate, very clearly, that stars placed at equal heights on, but on the opposite arms of the temperature curve, were suggested in former papers. For example, γ Cassiopeia (Cassiopeian, stage 3, *ascending*) there is a very marked difference in the intensity of the spectrum at the end of the curve, and α Persei (Perseian, stage 3, *descending*) spectrum of Procyon (Procyonian, stage 3, *ascending*) is very similar to the spectrum of α Persei at the same distance in the ultra-violet, the difference being only in the ultra-violet throughout. This point will be discussed further in a subsequent communication.

7. Conclusions.

(1) The present results affirm the equality of temperature of stars placed at equal heights on, but on the opposite arms of the temperature curve suggested by the Chemical Classification.

(2) The suggestion that the "genera" resulting from the Chemical Classification would require a subdivision into "species" is shown by the present results to be correct.

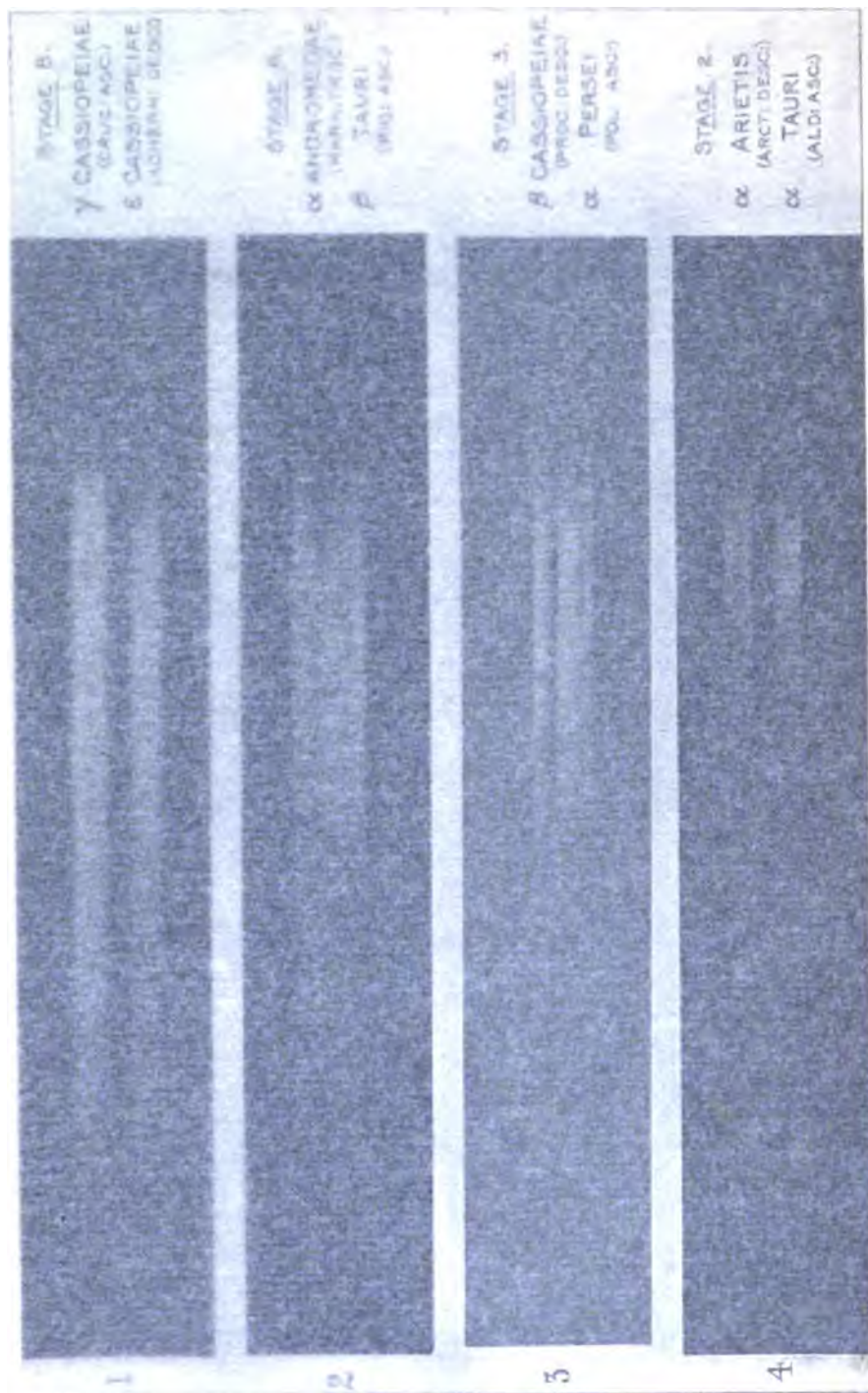
(3) The photographs obtained during the present investigation prove the existence of different absorbing conditions in the atmosphere of those stars which are equal in temperature but were placed on the opposite arms of the temperature curve.

My best thanks are due to Messrs. W. E. Relston and H. E. Gessner, who have secured the photographs discussed in the present paper, to Mr. J. H. Relston for assisting in the preparation of the paper, and to Mr. W. H. Relston, who prepared the enlargements shown on the accompanying plates.

8. Description of Plates.

No.	No. of negative.	Stars.	Temperature Curve.
1	65	γ Cassiopeia	Cassiopeian
		ϵ "	Antarian
2	68	α Andromeda	Andromedan
		β Tauri	Taurian
3	60	β Cassiopeia	Procyonian
		α Persei	Perseian
4	72	α Arietis	Antarian
		α Tauri	Aldebaran

The original negatives have been enlarged 38 times in making the reproductions.



These photographs also indicate, very clearly in some cases, the existence of the different conditions in the absorbing atmospheres of those stars placed on equal horizons, but on the opposite arms of the temperature curve, such as was suggested in former papers. For example, in the spectrum of α Persei (Polarian, stage 3, *ascending*) there is a very abrupt decrease of the general intensity of the spectrum at the end of the hydrogen series, whilst in the spectrum of Procyon (Procyonian, stage 3, *descending*), which extends to about the same distance in the ultra-violet, the decrease of intensity is gradual throughout. This point will be discussed further in a subsequent communication.

7 Conclusions.

(1) The present results affirm the equality of temperature of those genera placed at equal heights on, but on the opposite sides of, the temperature curve suggested by the Chemical Classification.

(2) The suggestion that the "genera" resulting from the Chemical Classification would require a subdivision into "species," is shown by the present results to be correct.

(3) The photographs obtained during the present research prove the existence of different absorbing conditions in the atmospheres of those stars which are equal in temperature but were placed on the opposite arms of the temperature curve.

My best thanks are due to Messrs. W. E. Rolston and H. E. Goodson, who have secured the photographs discussed in the present paper, to the former for assisting in the preparation of the paper, and to Mr. Wilkie, who has prepared the enlargements shown on the accompanying plate.

8. Description of Plate.

No.	No. of negative.	Stars.	Type.	Stage.
1	65	γ Cassiopeiæ	Crucian	} 8 { Ascending Descending
2	68	ϵ "	Achernian	
		α Andromedæ	Markabian	} 6 { Ascending Descending
		β Tauri	Rigelian	
3	60	β Cassiopeiæ	Procyonian	} 3 { Ascending Descending
		α Persei	Polarian	
4	72	α Arietis	Arcturian	} 2 { Ascending Descending
		α Tauri	Aldebarian	

The original negatives have been enlarged 3·8 times in making the reproductions.

*On Some Continuous Observations of the Rate of Dissipation of
Electric Charges in the Open Air.*

By C. COLERIDGE FARR, D.Sc.

(Communicated by Dr. C. Chree, F.R.S. Received February 23,—Read
March 9, 1905.)

During the latter part of 1902 and the early months of 1903 I resolved to take as many observations of the rates of dissipation of positive and negative electric charges as possible, and to continue them over the whole 24 hours of the day, and, when opportunity offered, over longer periods. There appeared to be little information regarding the rate of dispersion during the night hours. At about the same time that these observations were being made, Nilsson* was doing similar work at Upsala, and found a noticeable maximum value for atmospheric conductivity at about midnight.

The observations were made on the Canterbury Plains of New Zealand, at a station about 20 feet above sea-level and about five miles due west from the sea coast. The apparatus used was Elster and Geitel's† *Zerstreuungs-apparat*, and the formula of reduction used was that given by them, viz. :—

$$E = \frac{1}{t} \log \frac{V_0}{V} - \frac{n}{t'} \log \frac{V'_0}{V'}.$$

In this formula E is proportional to the conductivity of the gas surrounding the instrument—for positive or negative charges, as the case may be. The constant " n " = ratio of

$$\frac{\text{capacity without cylinder}}{\text{capacity with cylinder}}$$

was determined by me to be 0.47, as the instrument was always used, with the protecting cover. The cover was always at one height above the base of the instrument, and was set so as to be as nearly co-axial with the discharging cylinder as could be judged by eye. No attempt was made to determine the actual capacity of the condenser cylinder and protecting cover, which would be a somewhat variable quantity owing—

(1) to the differences on different days in attempting to cause the two to be co-axial;

(2) to a certain amount of looseness in the fit of the shank of the cylinder

* Nilsson, 'Science Abstracts,' vol. 6, abs. 560.

† Elster and Geitel, 'Terrestrial Mag.,' vol. 4, p. 213, *et seq.*

on to its hole. The value above given for "*n*" is the mean of several determinations made with different settings of the cover and cylinder. The individual values of "*n*" varied over about 0.03.

In reducing the observations by means of the above formula, as the relation between *E* and the conductivity was in any case, without knowledge of the capacity in absolute measure, one of proportionality merely, ordinary instead of Napierian logarithms were used. The voltages indicated by a given divergence of the leaves were taken from a table supplied by the makers of the instrument to Kew Observatory. The time was expressed in minutes.

In making the observations, the usual formal procedure of determining the leakage after every experiment was not adopted, as it was desired to obtain as many observations as possible in rapid succession. Thus the leakage was obtained only at fairly frequent intervals, and a curve drawn by which the ordinates of the curves representing *E* in the arbitrary unit explained above could be corrected.

Corresponding with the dispersion observations, observations were also made of the direction and intensity of the wind (Beaufort), the humidity, and the potential difference between a point about 10 feet above the surface of the ground and the earth. This was affected by the proximity of the building and was determined by a Kelvin portable electrometer and a water-dropper.

The leaves of the dissipation apparatus were read from a distance by the aid of a telescope, and at night the instrument was illuminated by a bull's-eye lantern attached to a pole. The lantern was only lighted during the actual minute or so that a reading was being taken.

A study of the curves so obtained led to several points of interest. In the first place it is evident that the conductivity of the air for both positive and negative electricity is very irregular, but the irregularities are such that on an average negative electricity is dispersed more rapidly than positive.

$$\text{Taking } q = \frac{\text{conductivity of air for -ve electricity}}{\text{conductivity of air for +ve electricity}},$$

six ordinary days, embracing several hundreds of observations, gave the following values for *q*, viz. :—

<i>q</i> = 1.2 March 1 and 2, 1903,	<i>q</i> = 1.12 September 1 and 2, 1902,
= 1.2 January 1 and 2, 1903,	= 1.27 February 1 and 2, 1903,
= 1.12 January 15 and 16, 1903,	= 1.06 December 15 and 16, 1902,

giving an average of *q* = 1.16.

Though this is so persistently as an average, yet on several occasions for

some hours together during these six days, positive electricity was dissipated the more rapidly. Thus this occurred from noon to 5.30 P.M. on January 1, and again from 6.30 to 9.30 A.M. on the morning of the next day, January 2. During these intervals there was no reversal of the sign of the atmospheric potential as indicated by the electrometer. On the first of these occasions the average value of q for the period was 0.85, and on the second 0.86. Similarly, on January 15, 1903, between 12 noon and 3.30 P.M., positive charges were dissipated the more quickly. During the interval the average value of q fell to 0.6, and the potential at the terminal of the water-dropper fell from +50 volts at 12.30 P.M. to -40 volts at 3 P.M., rising again at 3.45 P.M. (by which time negative electricity was again being discharged the more quickly) to +65 volts. On September 1, 1902, also at 5 P.M., q was for a very short time 0.4, whilst the potential of the water-dropper fell from +90 volts at 3.30 P.M. to -717 volts at 5 P.M., rising again to -70 volts at 6.30 P.M. From then on till noon next day, when the observations terminated, the potential remained positive, as is usually the case, but at 4.30 A.M. on September 2 the positive charge again became dissipated more quickly, and continued so till 10 A.M. During this interval q was 0.68. On February 1, 1903, positive electricity was dissipated the more quickly from 3 P.M. till 7 P.M., with no reversal of the sign of the atmospheric potential. During the interval the average value of q was 0.87. Between 6 and 6.30 P.M. on December 15, 1902, q (from a pair of observations only) became 0.8 with no reversal of atmospheric potential, whilst next morning, during very heavy rain at 6 A.M., $q = 0.7$ for a short time, with a reversal of potential sign at 5 A.M. -80 volts, and at 6.30 A.M. -180 volts. Summing up these we find:—

January 1, 1903.....	$q = 0.86$, no reversal atmospheric charge
September 1, 1902.....	$= 0.68$ " " "
February 1, 1903	$= 0.87$ " " "
December 15, 1902 ...	$= 0.8$ " " "
January 15, 1903	$= 0.6$, reversal atmospheric charge
September 1, 1902.....	$= 0.4$ " " "
December 16, 1902 ...	$= 0.7$ " " "

This apparently indicates that a low value for q is, as might be expected, accompanied with a reversal of sign of the atmospheric charge. On the other hand, on March 2, at 6.30 A.M., the potential became -185 volts with q about unity.

Again, considering these six days only as being more typical of ordinary

conditions than two others I shall refer to, we find there is distinct evidence of a double maximum and minimum value for the conductivity of the air for charges of both signs. Thus on the following dates the maxima and minima are well marked at the following approximate times:—

	max.	min.	max.	min.
March 1 and 2	5 P.M.	9 P.M.	3 A.M.	7 A.M.
January 1 and 2.....	12 noon	6 P.M.	3 A.M.	7 A.M.
January 15 and 16.....	12 noon	6 P.M.	3 A.M.	9 A.M.
September 1 and 2.....	2 P.M.	5 P.M.	1 A.M.	9 A.M.

Of the two other days, viz., February 1 and 2 and December 15 and 16, the former exhibits no distinct maxima and minima, but a strong south-west gale was blowing during most of the period of observation; and the latter is incomplete in the night hours owing to faulty insulation of the instrument due to rain. The four days above were fine.

The observations made on February 1 and 2 during the south-west gale gave a much higher value for the conductivity of the air for both positive and negative charges than upon the other four complete days. Thus, in the arbitrary units chosen, the mean conductivity for this day was for positive charge 0·00694 and for negative 0·00880, whilst the average of the other four was for positive 0·00330 and for negative 0·00375. Similarly, on March 1 and 2, also during a south-west wind of moderate strength, the conductivities were higher than the average, viz., for positive charges 0·00475 and for negative 0·00569. Since the wind on these two days of high mean conductivity was in the same direction, south-west, and also stronger than on the other three, there is only a slight amount of evidence to indicate that the excessive conductivity is due to the strength rather than to the direction of the wind.

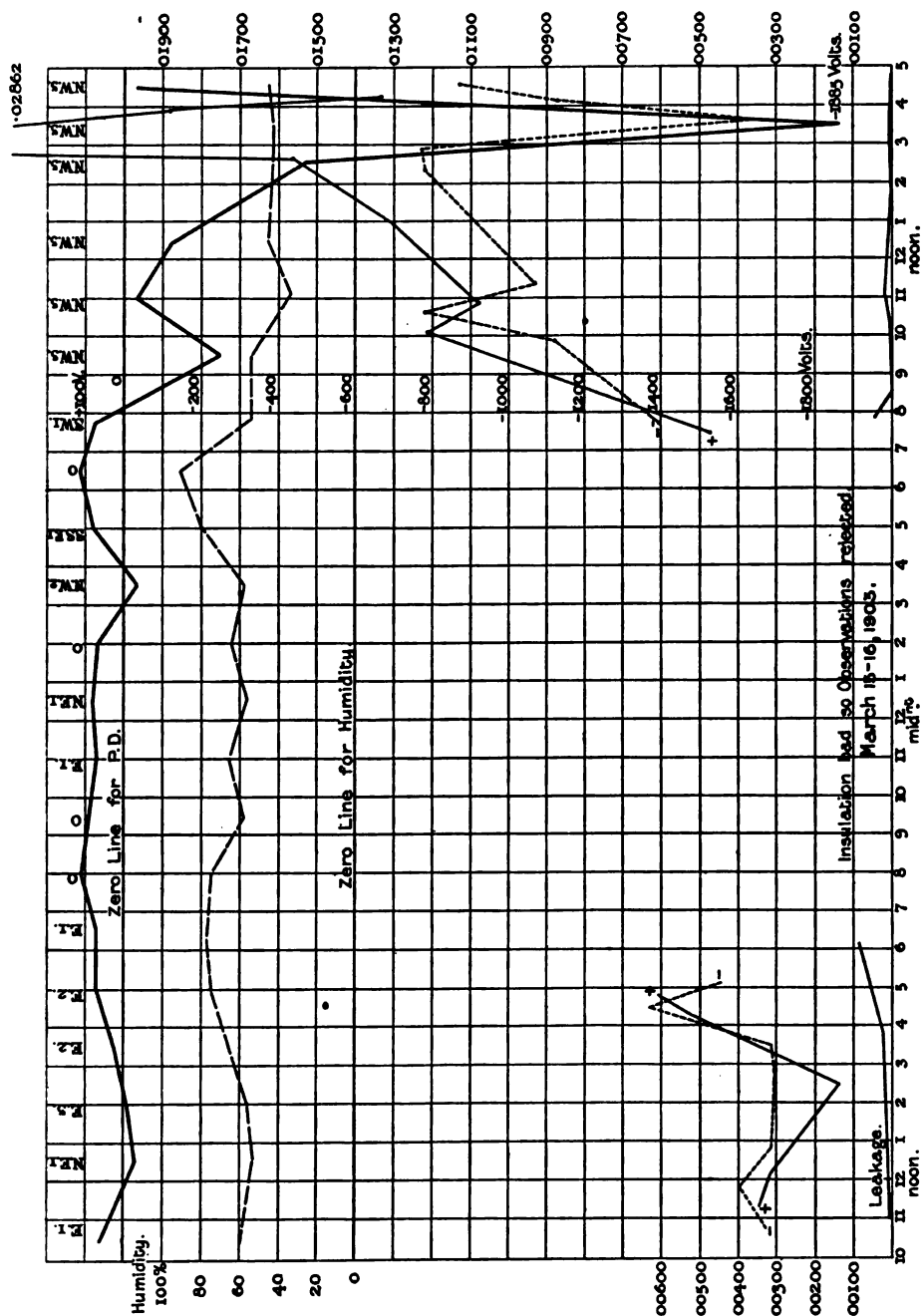
I am unable to discover in these curves any connection between the humidity of the air and its electrical condition.

I now come to two days as yet not mentioned, viz., February 18, on which observations were specially made from 11 A.M. to 5 P.M., and March 16, when observing conditions were good from 7 A.M. till 5 P.M. On the first of these two days a strong gale from the north-west—a “nor’wester” as they are generally called here—was blowing at the time the observations were begun, whilst on the latter, at 6.30 A.M., the wind was calm. At 8 A.M. there was a light south-west wind, and at 9.30 it was blowing strongly from the north-west with a characteristic falling barometer. The wind remained north-west during the rest of the day. These “nor’westers” are very well known and,

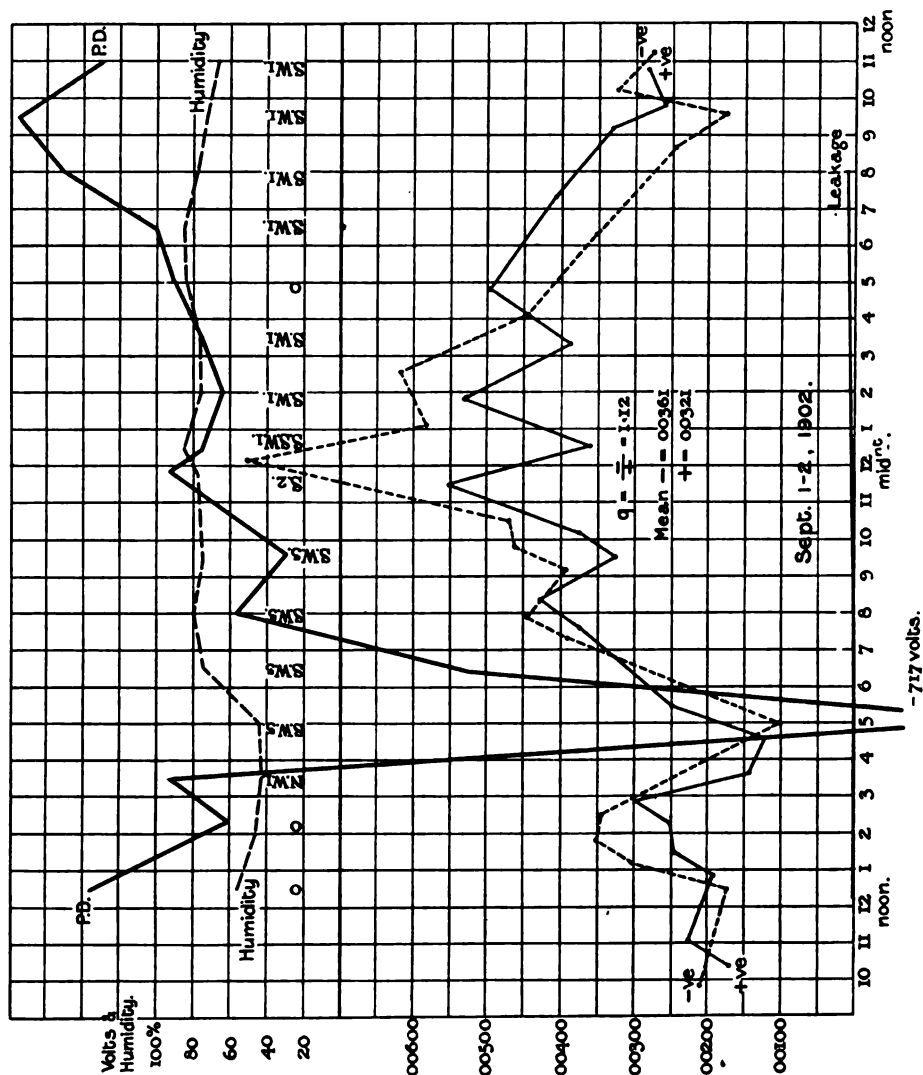
by some people, rather dreaded winds. Blowing over a high range of mountains reaching 7000 feet, they deposit their moisture on the western slopes, though the rain often extends to the eastern side of the mountains. In Christchurch, and for some distance westward of it, these winds are invariably dry and hot. They are of the nature of "Foehn" winds, and have a very depressing effect upon most people, though I have met some who say they like them.

Though the days I am describing are the only two of the class upon which, so far, I have been able to take dissipation observations, yet potential observations on them indicate that the general character of these winds is that they are negatively charged relatively to the earth, which is contrary to the usual condition. On both of these days the dissipation curves show marked peculiarities. The earliest observation, at 11.15 A.M. on February 18, gave $q = 0.4$ with a negative potential difference between water-dropper and earth of, -300 volts at 10.20 A.M., -150 volts at 11.40 A.M., and -50 volts at 12.45 P.M. These three values at the times indicated lie on a straight line and appear to show that the potential of the water-dropper was rising approximately uniformly with the time. Corresponding with this rise of potential there is also a marked rise in the value of q , which at 12 noon had risen to 0.8 and at 2.30 P.M. was 1.5 , by which time the "nor'wester" had practically blown itself out, and the potential of the water-dropper was zero. After this the value of q sank again to approximately unity, the ordinary positive atmospheric charge established itself and the wind blew lightly from the south-west.

The curves corresponding to March 16 (see the figure) are of a precisely similar character, but here the whole history of the wind is apparent. At 7.30 A.M. the wind was light south-west, $q = 1.3$, potential of water-dropper $+90$ volts. At 9.45 A.M., wind north-west, strong, $q = 0.7$, potential -250 volts. At 10.30 A.M., wind north-west, strong, $q = 1.1$, potential -100 volts approximately (interpolated). From this hour the north-west wind seemed to have thoroughly established itself. The values of q became less and less, the curves indicating the conductivity of the air for positive and for negative charges diverging rapidly, that for positive reaching a high value whilst the negative curve reached remarkably low values. Thus at about 3 P.M., the point of maximum divergence of these curves, in the arbitrary units chosen for the conductivities, that for positive electricity was 0.029 , whilst the conductivity for negative electricity was only 0.0037 , giving a value for q of 0.12 . Corresponding with this extremely low value for q the potential reached at very approximately the same time its greatest negative value, viz., -1885 volts. After this the value of q increased, the curves representing the



conductivities converging—that for positive electricity coming down whilst the negative conductivity increased. Corresponding with this increase of q the negative potential of the water-dropper decreased, until at 4.30 P.M.



$q = 0.94$, potential -30 volts, wind still strong from north-west; but it dropped shortly after this.

It may be possible to account for the peculiar character of these two north-west winds (and though I have so far been unable to obtain further observations, I expect to find it common to the wind) in this way. The wind,

as stated, blows over a mountain range. These mountains may rob the air of positive ions owing to the denser negative charge on the peaks.* Thus the air may come over the Canterbury Plains with an excess of negative ions, giving it great conductivity for positive charges and conferring on it its own characteristic highly negative charge.

In the curves reproduced the lowest line of all represents the actual leakage, the faint dotted line the variations in conductivity for negative charges, and the faint full line those for positive charges. These are all in the same arbitrary units explained above. The heavy full line represents the variations in the potential of the water-dropper referred to an origin higher up in the paper. The broken line represents the relative humidity. The letters E, N.E., etc., denote the direction of the wind, and the attached numerals its intensity on Beaufort's scale.

My thanks are due to Mr. H. F. Skey, B.Sc., for aid in making the observations on September 1, and to Mr. F. Sandford for help on January 15, February 1 and 18, and March 1 and 15. For the opinions expressed, and for the observations on December 15 and January 1, I alone am responsible, as I am also for the accuracy of the reductions.

* See also Elster and Geitel's results at Wolfenbüttel.

Atmospheric Electricity in High Latitudes.

By GEORGE C. SIMPSON, B.Sc.

(Communicated by Arthur Schuster, F.R.S. Received February 17,—

Read March 2, 1905.)

(Abstract.)

The recent work of Elster and Geitel, Ebert and others, has added three new factors to the data for the study of atmospheric electricity, namely:— The rate at which the permanent charge on the surface of the earth is being dissipated into the atmosphere, the state of ionization of the air, and the amount of radio-active emanation in the lower regions of the atmosphere. These three factors have been carefully studied in the temperate zone. With the idea of extending our knowledge of them into the Arctic regions, I was granted permission by the Commissioners of the 1851 Exhibition Scholarship to undertake a year's work in the Lapp village of Karasjok ($69^{\circ} 17' N.$; $25^{\circ} 35' E.$; 129 metres above sea level, and about 200 miles south of the North Cape). The work undertaken consisted of the following:—

1. By means of a Benndorf self-registering electrometer to obtain daily curves of the potential gradient, and from these to calculate the yearly and daily variation.
2. To make systematic observations of the dissipation by means of Elster and Geitel's instrument.
3. To make corresponding measurements of the ionization with Ebert's apparatus.
4. To measure the amount of radio-active emanation in the atmosphere.
5. To investigate, as far as possible, the influence of the aurora on the electrical conditions of the atmosphere.

The chief results obtained are, shortly, as shown in Table I (p. 161).

In the table the following units are used:—

The *Potential Gradient* is expressed in volts/metres as observed over a level plain.

The *Dissipation* is expressed as the percentage of charge lost by a charged body in one minute when freely exposed to the air. The dissipation of a positive charge is represented by a_+ , and that of a negative by a_- , the ratio a_-/a_+ being written q .

The *Ionization* is given in terms of the number of electro-static units of free ions, of one sign, in a cubic metre of air. The symbol I_+ is used to

represent the positive ionization, I_- the negative ionization, and r the ratio I_+/I_- .

It will be seen that the yearly course of the potential gradient in Karasjok is in accordance with the general rule for the Northern Hemisphere: rising rapidly from October to February, when it reaches a maximum, then falling

Table I.—Yearly Variations.

Months.	Potential gradient, volts/metres.	Dissipation.			Ionization.		
		a_+ .	a_- .	q .	I_- .	I_+ .	r .
October	121	2·21	2·65	1·20	0·34	0·40	1·18
November ..	167	3·20	3·43	1·07	0·25	0·35	1·40
December ...	175	2·13	2·53	1·19	0·28	0·39	1·39
January	199	1·98	2·33	1·18	0·25	0·26	1·04
February ...	209	1·37	1·47	1·08	0·20	0·24	1·20
March	191	2·79	3·74	1·34	0·28	0·32	1·14
April	131	3·78	4·38	1·16	0·31	0·38	1·22
May	103	4·41	4·76	1·08	0·35	0·40	1·18
June	90	4·24	4·68	1·10	0·37	0·41	1·09
July	98	5·25	5·97	1·13	0·42	0·46	1·10
August	93	4·32	4·94	1·14	0·45	0·51	1·13
September...	93	4·28	4·89	1·14	0·42	0·46	1·08

more rapidly until the end of May, after which it remains constant until the winter sets in again during October.

The course of the dissipation is exactly opposite to that of the potential gradient, the curve representing the two being almost mirror images of one another. The yearly course of the ionization consists of a nearly linear six months' fall, from the beginning of September to the end of February, followed by a similar six months' rise, from March to the end of August.

Daily Variations.

The daily course of the potential gradient for the whole year consists of a single period having a minimum about 5 A.M., and a maximum about 9 P.M.

Observations of the dissipation and ionization were made three times a day: morning from 8 to 9 A.M.; midday from 12 to 1; evening from 6 to 7 P.M. From the observations, the following facts as to the daily variation can be found.

Dissipation.—During the winter and spring the morning observations

show a slightly higher dissipation than the midday, while, on the contrary, during the summer and autumn, the midday values are the higher. For the whole year the dissipation is slightly higher at midday than earlier in the morning, while the evening observations show the lowest dissipation of the three. The value of the ratio r for nine months shows a daily period, being lower at midday than at either the morning or evening observations.

Table II.—Daily Course of the Potential Gradient.

	A.M.	P.M.		A.M.	P.M.
12 to 1.....	115	147	6 to 7	113	180
1 „ 2.....	102	151	7 „ 8	121	189
2 „ 3.....	92	151	8 „ 9	131	194
3 „ 4.....	87	152	9 „ 10	140	185
4 „ 5.....	84	153	10 „ 11	138	169
5 „ 6.....	95	165	11 „ 12	144	142

Ionization.—The daily period of the ionization is not so pronounced as that of the dissipation; but the ionization is slightly lower in the evening than in the morning or at midday during the whole year. There is practically no difference between the midday and morning ionization. The daily period of the ratio q is a steady rise from the morning to the evening; in this respect the ionization does not correspond with the dissipation.

Interrelation of the Ionization, Dissipation, and Potential Gradient.

Both the dissipation and ionization greatly influence the potential gradient. Low values of ionization and dissipation are accompanied by high values of the potential gradient, and *vice versa*.

As the potential gradient rises both the ratios q and r become greater.

For any given wind strength, the observations show that the dissipation, as measured by Elster and Geitel's instrument, is a linear function of the ionization.

Relation between the Meteorological and Electrical Condition of the Atmosphere.

Wind.—As is to be expected, the dissipation increases greatly with the wind strength. The ratio q shows a steady decrease as the wind strength increases.

Temperature.—Both the ionization and dissipation become much less as

the temperature goes down. With temperatures between 10° and 15° C., the dissipation is 4.95 per cent. and the ionization 0.44; while with temperature below -20° C., these become 0.83 per cent. and 0.17 respectively. As is to be expected from the relation already described between potential gradient, dissipation, and ionization, the potential gradient increases as the temperature falls.

Relative Humidity.—With rising relative humidity, the dissipation falls rapidly, and the ratio of negative to positive dissipation (q) increases. When the whole year is taken into account, the same result is found for the ionization; but for the winter and summer six months, taken separately, the effect of the humidity of the air on the ionization is not apparent.

The Aurora and the Electrical Conditions of the Atmosphere.

No relation whatever could be detected between the aurora and the electrical conditions of the atmosphere. The most careful watching of the electrometer needle revealed no variation of the potential gradient with variations of the aurora.

Radio-Activity.

Measurements of the radio-activity were made by Elster and Geitel's method,* and their arbitrary unit used in expressing the results. Observations were made at four different times of the day—viz., from 3 to 5 A.M., from 10 to 12 A.M., from 3 to 5 P.M., and from 8.30 to 10.30 P.M. During the year 420 observations were made in Karasjok and 78 in Hammerfest.

A most distinct yearly course of the radio-activity was found, the maximum falling in mid-winter and the minimum in mid-summer.

Table III.—Yearly Course of the Radio-activity.

	Nov. and Dec.	Feb.	Apr.	May and June.	July and Aug.	Sept.
A, mean ...	129	127	55	47	80	123
A, max. ...	432	366	210	204	270	390

The radio-activity has also a very pronounced daily course, the maximum falling in the early hours of the morning and the minimum about midday.

Table IV.—Daily Course of the Radio-activity.

	Early morning, 3 to 5 A.M.	Morning, 10 to 12 A.M.	Afternoon, 3 to 5 A.M.	Evening, 8.30 to 10.30.
A, mean	162	58	62	92

* 'Phya. Zeit.,' vol. 4, p. 526, 1903.

There is a distinct connection between the radio-activity and the meteorological condition of the atmosphere.

The radio-activity increases as the temperature falls, rises as the relative humidity rises, decreases with increasing wind strength, and is greater with a falling than a rising barometer. All these facts support Elster and Geitel's theory that the source of the radio-active emanation in the atmosphere is the soil of the ground. Those meteorological conditions which prevent the air immediately above the ground from ascending tend to increase the radio-activity; on the contrary, all those conditions which cause a rapid circulation of the air greatly reduce the radio-activity when measured in the lower atmosphere.

As stated above, measurements of the radio-activity were also made in Hammerfest. The observations extended over four weeks. The mean values were found to be considerably lower than at Karasjok. The most important result of the Hammerfest measurements was the great difference in the radio-activity of the air from the sea and that from the land, as shown in the following table:—

Table V.—Radio-activity and Wind Direction in Hammerfest.

	North.	South.	West.
A, mean	8	72	4
A, max.	20	250	10

Note on Fluorescence and Absorption.

By JOHN BUTLER BURKE, M.A.

(Communicated by Professor Larmor, Sec. R.S. Received March 13,—Read March 30, 1905.)

In a paper "On the Change of Absorption produced by Fluorescence,"* I described the existence of a very remarkable difference in the absorption of the fluorescent light of uranium glass, when in the luminous and non-luminous states. This difference I have attributed† to a temporary change in the structure or chemical composition of the body when exposed to the influence of the exciting light; and I have been led to suppose that it is due to the formation of new atomic connections which give rise to new frequencies during the period of luminosity. These I regarded as the result of the formation of unstable molecular aggregates by the more refrangible or exciting rays; and the luminosity or fluorescence, as the radiation which results from the breaking down of such unstable molecular groups. As in the case of photographic action, some chemical change appears to be produced by the blue and violet rays; the two cases differing, from the physical point of view, merely so far as the molecular aggregations, instead of remaining fixed, rapidly disintegrate, radiating intensely at the same time the energy which was stored up in their formation. Thus the luminosity itself is but the visible manifestation of the building up and breaking down of what are probably complicated molecular agglomerations.

In their very interesting and important paper on this subject,‡ Messrs. Nichols and Merritt have shown that the phenomenon of the change of absorption depends upon the intensity of the fluorescence. They find that a saturation effect takes place as the intensity of the luminosity increases, so that the change of absorption reaches a maximum with a certain intensity of the fluorescent light.

In my experiments the transmitted light, the absorption of which was measured, was of precisely the same frequency as that emitted by the absorbing body; its source being another similar fluorescent substance likewise in a state of fluorescence. Messrs. Nichols and Merritt, however, have found that

* 'Phil. Trans.,' A, 1898.

† 'Brit. Assoc. Report,' Belfast, 1902 (cf. Sir G. G. Stokes, 'Math. and Phys. Papers,' vol. 3 (1901), p. 310; also "On the Discharge of Phosphorescence," 'Roy. Soc. Proc.,' vol. 34, 1882, p. 63, or 'Papers,' vol. 5, p. 118).

‡ 'Physical Review,' December, 1904, p. 396.

the same effect occurs when the source of the transmitted light is an acetylene flame. Although this includes rays in the more refrangible part of the spectrum, which increase the fluorescence of the absorbing body and thereby diminish its apparent coefficient of transmission, yet, provided this factor remains constant, the variation in the absorption of the light from the flame, corresponding to that of the fluorescence due to some other exciting source, should still take place and be noticeable, if the change is considerable, as I found it to be. And they have found no difficulty in observing the result, as I have done.

The object of this note is to call attention to M. Camichel's paper on Fluorescence in the '*Comptes Rendus*' (January 16, 1905), as he obtained a negative result. This may have been due to the feebleness of the fluorescence on the one hand, and on the other to the fact that the precaution which he takes of using a fluorescent screen, 7 cm. in thickness, to cut off the more refrangible rays from the flame (a precaution which, as I have said, is unnecessary) ought also to stop the greater portion of the rays, the absorption of which by another but similar body, he desires to detect. The parallelopiped of uranium glass, 7 cm. in length, must itself fluoresce, and in so doing, if the effect he seeks occurs, absorb the very rays whose absorption later on by a cube of uranium glass he proposes to measure. Furthermore, the fluorescent spectrum of uranium glass is composed of several bands, and these, I think, in turn are not continuous but made up of finely divided smaller bands or lines.

The prevalent idea that the spectrum of fluorescent and phosphorescent bodies is continuous is, I think, erroneous; for whenever I have been able to get the luminosity of sufficient brightness, the spectrum which, when the light was feeble, seemed continuous, was found distinctly to be made up of finer bands; whilst when the intensity was diminished the distinctly band-like spectrum was once more found to be dimmed and become continuous. Therefore if, by any means, the light of precisely the same period as the fluorescent light be sifted, or removed, from the spectrum of the light transmitted through uranium glass, we should not expect to get any variations in the absorption corresponding to the changes in the body during the fluorescent state.

M. Ch. Ed. Guillaume and M. A. Cotton, who have taken much interest in the bearing of Kirchhoff's law on fluorescence, have written to me expressing their concurrence with this aspect of the question.

I should like to add, in conclusion, that there does not seem to be any reason to suppose, as M. Camichel implies, that the vibrations of the fluorescent light should not be linear, when the absorption depends on the intensity of the

fluorescent light. It is true that it would not depend upon the amplitudes of the vibrations; but if new free periods are excited as I have described, the intensity and the absorption would both depend upon the number, and the duration of the periods thus produced, and it is this which, I think, the change of absorption in fluorescence most distinctly proves.

The Direct Synthesis of Ammonia.

By EDGAR PHILIP PERMAN, D.Sc., Assistant Professor of Chemistry at
University College, Cardiff.

(Communicated by Principal E. H. Griffiths, F.R.S. Received January 3, and in revised form, March 4,—Read March 30, 1905.)

It was shown in a recent paper on "The Decomposition of Ammonia by Heat,"* that ammonia is decomposed almost (if not quite) completely when heated in a porcelain vessel at about 800° to 1100° , and that there is no sign of equilibrium between the ammonia and its decomposition products at any of the temperatures employed, 677° to 1111° .

In order to discover if there is any such state of equilibrium, it was thought better to attempt to reach that state by synthesising ammonia instead of decomposing it, as the testing for and estimation of the ammonia could then be carried out with much greater accuracy.

Preparation of the Mixed Gases.—In the first series of experiments, the mixture of nitrogen and hydrogen was made by passing ammonia gas, from a strong aqueous solution, through a red-hot iron tube heated in a gas furnace, and the resulting gases were collected in a large gasholder and stored over dilute sulphuric acid. It may be objected to this method of preparation that carbon monoxide, hydrogen, and other gases would percolate through the iron, and contaminate the product obtained. In order to test this point, a careful analysis of the gases was made, with the result that no carbon monoxide could be detected by the blood test; no carbon dioxide was found after exploding the gases with oxygen; and the ratio of nitrogen to hydrogen was found to be correct. The mixture of gases made by this method will be referred to as "Mixed Gases I."

It was thought, nevertheless, that traces of foreign gases might have escaped detection, and might possibly have influenced the results. Consequently a second series of experiments was carried out with a mixture of

* 'Roy. Soc. Proc.,' vol. 74, p. 110, 1904.

nitrogen and hydrogen made in an entirely different way. Nitrogen gas was made by heating gently a solution of equivalent quantities of ammonium chloride and sodium nitrite, and hydrogen was prepared from a concentrated potash solution heated with metallic aluminium, the gas being passed through two Drechsel flasks containing potassium permanganate solution.

Each gas was stored in a gasholder, and a mixture of the two was then made, in the proportion of 1 volume nitrogen to 3 volumes hydrogen, in a third gasholder. The volume of gases was measured by the volume of water drawn off, due regard being paid to the "head" of water. This mixture will be called "Mixed Gases II."

Attempted Synthesis by Heat. (Mixed Gases I, and II, separately).—The mixture was proved to be free from ammonia by testing with Nessler's solution. It was then passed through a hard glass tube heated in a combustion furnace. Glass was chosen as likely to have no chemical action on ammonia or its constituents. The temperature was varied from about 600° to 1000° C. The resulting gases were bubbled through dilute hydrochloric acid solution; this was afterwards made alkaline with potash, and Nessler's solution added. The result was that *no ammonia could be detected*, whatever the temperature or state of gases as to moisture.

In some experiments the mixture was freed from traces of oxygen by bubbling through alkaline pyrogallate solution, and then dried by strong sulphuric acid; in other experiments these precautions were omitted, but the result was always the same, and was obtained many times.

The experiment was varied by filling a porcelain globe with nitrogen and hydrogen (Mixed Gases I), and heating it in a furnace to a bright red heat for about 1½ hours. The gases were then tested for ammonia in the usual way, but not a trace was found. We may conclude, therefore, from these experiments, that ammonia cannot be synthesised from nitrogen and hydrogen by heating in vessels of glass or porcelain, or that, if it is formed, it is not in sufficient quantity to be detected by Nessler's solution.

Synthesis by Heat in the Presence of Iron. (Mixed Gases I).—Some of the mixed gases were then passed through an iron tube heated to redness, or in some cases a glass tube containing iron nails, and it was found that, when moisture was present, traces of ammonia were formed; if, however, care was taken to exclude moisture by passing the gases through alkaline pyrogallate solution and sulphuric acid, and reducing any iron oxide, then no ammonia could be detected. This result was obtained also by Ramsay and Young.*

In order to form an idea of the amount of ammonia produced, known

* 'Chem. Soc. Journ.,' vol. 44, p. 88, 1884.

volumes of the mixed gases were passed through a hard glass tube packed with "French nails," and the ammonia was estimated by Nessler's solution, as in the method used in water analysis. The following results were obtained:—

Vol. of mixed gases. c.c.	Approximate rate. litres per hour.	Ammonia. milligrammes.
500	10	0.03
500	10	0.06
250	3	0.08
250	3	0.10

No ammonia could be detected in any case unless the iron was at a bright red heat, about 800° to 900°. With Mixed Gases II:—

Time. ' "	Vol. of mixed gases. c.c.	Ammonia. milligrammes.
8 20	250	0.20
2 45	250	0.20
0 42	250	0.17

It will be noticed that the maximum amount of ammonia was formed when the gases were passed at the middle rate, indicating that the mixture had come into equilibrium. More than twice as much ammonia per litre of mixed gases was formed in this series as in the first, and it appeared to be formed at a lower temperature. Moreover, when the gases were carefully dried by sulphuric acid, traces of ammonia were still found. Whether this difference was due to greater purity of the gases or to any other variation in the conditions (*e.g.*, the new French nails) I am unable to say.

My attention has been called to a paper by Haber and van Oordt* in which some very similar experiments are described. The proportion of ammonia formed in the experiments of these investigators was about 0.2 to 1000 possible (if completely converted), which is considerably less than obtained by me, but the temperature and other conditions were different in the two cases.

Haber and van Oordt have attempted to find the dissociation constant at different temperatures, but it appears to me that the available data are entirely insufficient for the purpose. Moreover, the part played by the iron is not yet completely understood.

My experiments show that the quantity of ammonia formed depends on the amount of moisture present, but Haber and van Oordt appear to have overlooked this point, and say simply that their gases were dry.

* *Zeita. für anorg. Chemie*, vol. 43, p. 111, 1906.

Synthesis by Heat in the Presence of other Substances.—Similar experiments were made with a number of other metals. Copper, zinc, nickel, cobalt, palladium, aluminium, and magnesium, all gave traces of ammonia, but usually less than iron. Platinum sponge yielded traces, whilst platinised asbestos and platinum foil produced very minute and scarcely perceptible quantities. Zinc and copper in contact gave no more than when present separately. In all these cases, which were made with "Mixed Gases I," no attempt was made to exclude moisture.

Effect of Large Surface.—(Mixed Gases I.) The following substances were selected in order to test the influence (if any) of large surfaces, on the synthetical formation of ammonia: pipe stems, pumice, broken porcelain, asbestos. A hard glass tube was packed with the substance, and the experiment conducted in the usual way. As the result, traces of ammonia were found in each case, except with the porcelain. All these substances, except the porcelain, contained a notable quantity of iron, and I believe that it is owing to its presence that the ammonia was formed. The porcelain was from a broken globe, see former paper.* The pipe-stems altered in colour, under the influence of the gases, from a yellowish tint to a dull grey, which I ascribe to the reduction of the iron present. Although my conclusion may be questioned, I believe that (in this case) the extent of surface has no effect, unless the substance with which the gases are in contact reacts chemically with them.

Synthesis by Explosion.—It was noticed that if an explosion of the mixed gases and air took place in the hard glass tube, traces of ammonia were formed, and the effect was further investigated by exploding the gases with oxygen in a eudiometer and testing the resulting gases for ammonia.

The following are the results:—

Mixed gases.	Oxygen.	Result.
c.c.	c.c.	
10·5	2	Trace of ammonia
15	5·2	ditto (but less)
16	3·5	ditto
16·3	3·4	ditto
16	9	ditto (but less)

It will be seen that the quantity of ammonia formed diminishes if the oxygen is in excess. The quantities were very small, but nevertheless considerably greater, in proportion to the volume of gases taken, than those

* *Loc. cit.*

produced by the action of iron. Similar effects have been noticed by other investigators.*

Synthesis by Sparking.—It is well known that ammonia can be synthesised in small quantities with the aid of high potential electric discharges, and I have now attempted to bring the gases into a state of equilibrium during sparking, *i.e.*, into such a state that the rate of decomposition is equal to the rate of formation of the ammonia, and to reach that condition from each direction.

Mixed Gases I. The experiments were carried out in a glass bulb of about 250 c.c. capacity, provided with two tubes and stop-cocks, and with platinum wires for sparking, the sparking distance being about 25 mm

The bulb was placed in a thermostat and maintained at a temperature of 40° C., it was filled with the mixed gases, and the platinum wires connected with the terminals of an induction coil capable of giving an 8-inch spark.

After the sparking the gases were aspirated into dilute hydrochloric acid solution and nesslerised. The various results are put together in the following tables :—

Pressure.	Time of sparking. mins.	Ammonia formed. milligrammes.	Remarks.
Atmospheric	5	0·02	moist gases
"	15	0·06	"
"	15	0·02	very thin spark gases dried by H ₂ SO ₄
"	5	0·02	
"	10	0·03	
"	15	0·06	
"	20	0·07	"
"	30	0·10	"
"	45	0·10	"
2 atmospheres	60	0·19	"
"	30	0·19	"

From these results it will be seen that :—

(1) Under atmospheric pressure equilibrium (as before defined) was reached when 0·1 milligramme ammonia had been formed.

(2) Under a pressure of two atmospheres equilibrium was reached when 0·19 milligramme was present.

(3) The amount of ammonia formed depends on the quantity of electricity passing, thus a very thin spark produced only one-third as much ammonia as a "fat" spark in the same time.

* See Watts' Dictionary, 1st ed., Art. "Ammonia."

Decomposition of Ammonia by Sparking.—Attempts were made to reach the same equilibrium points by starting from the opposite end of the reaction. It was found to require long sparking before equilibrium was nearly reached. The following are the results:—

Pressure.	Time of sparking. hrs.	Ammonia remaining. milligrammes.
Atmospheric, allowed to blow off every few minutes	2.5	0.13
Atmospheric, rising to two atmos. at end	5	4.2
Two atmos., commencing with a mixture of N and H (1 : 3), and 2 per cent. NH_3	2	0.56
Two atmos., commencing with a mixture of N and H (1 : 3), and 1 per cent. NH_3	2.5	0.32

At atmospheric pressure decomposition was rapid, and the equilibrium point was very nearly reached, synthesis giving 0.10 milligramme and analysis 0.13 milligramme. When the volume was kept constant, decomposition was very slow and the point of equilibrium was approached only by starting a long distance from the beginning of the decomposition. Starting with a mixture containing 1 per cent. of ammonia, after $2\frac{1}{2}$ hours' sparking, 0.32 milligramme ammonia remained instead of 0.19 milligramme by the synthetical method.

Mixed Gases II.—In this series the length of the spark was 11 mm., and the capacity of the globe 262 c.c. At the conclusion of the experiment the gases were pumped out through dilute acid. The temperature was $39^{\circ}8$ C.

In primary coil.

Time. mins.	Current. ampères.	Voltage.	Ammonia. milligrammes.
15	2	4	0.08
30	2	4	0.30
15	1.5	4	0.25
30	5.5	4	0.44
45	5.5	4	0.37
22.5	5.5	4	0.41
15	2.75	2	0.07
Decomposition of ammonia by sparking.			
68	5.5	4	0.41

From these results it is seen that—

(1) Equilibrium was reached in about 22 minutes, the gases then containing 0.41 milligramme ammonia. On sparking ammonia at atmospheric pressure exactly the same point of equilibrium was reached.

(2) More ammonia is formed than in the first series, owing to the shorter spark; also the rate of decomposition and the rate of formation are quicker.

(3) Other conditions remaining the same, the amount of ammonia formed is roughly proportional to the current strength.

(4) If the current strength remains the same, the quantity of ammonia formed is much influenced by the voltage. (It must be remembered that the electrical measurements here mentioned are those of the primary coil.)

Since writing the above, I have discovered that Berthelot carried out experiments of a somewhat similar nature. He found that, starting either with ammonia or with nitrogen and hydrogen, sparking left finally a minute quantity of ammonia which was "of the same order" in the two cases.* Using the silent discharge, he obtained the same point of equilibrium, starting from either direction, viz., a mixture containing 3 per cent. ammonia. Reference should be made also to the work of Hemptinne, who has investigated the synthesis of ammonia under various conditions.†

Summary.

(1) So far as can be shown by one of the most delicate tests known to chemists, ammonia cannot be synthesised by heat (except under special conditions specified below). The decomposition of ammonia by heat may, therefore, be regarded as an irreversible reaction.

(2) Ammonia may be synthesised in small quantities from its constituent elements (a) by heating with many of the metals; (b) by exploding with oxygen; (c) by sparking. These are reversible reactions.

(3) It would appear that the synthesis of ammonia is effected only when the gases are ionised; the ionisation would be brought about by sparking, or by the high temperature of an explosion of hydrogen and oxygen. The immediate decomposition of the ammonia formed would be prevented by its sudden cooling. The metals in the presence of moisture also produce "nascent" or ionised hydrogen.

(4) It does not appear that nitrides of the metals form an intermediate stage in the formation of ammonia, for it was found that metals readily forming nitrides, *e.g.*, magnesium, did not produce more ammonia than the others.

* 'Mécanique chimique,' vol. 2, p. 358, 1879.

† 'Bull. Acad. Roy. Belgique,' 1902, p. 28.

(5) There is a close analogy between ozone and ammonia with regard to their synthesis and decomposition; both are formed by sparking, and both are completely decomposed by heat.

In conclusion, I wish to express my thanks to Mr. G. A. S. Atkinson, B.Sc., and to Mr. J. H. Davies, B.Sc., for valuable assistance rendered during the earlier and later portions of the work respectively.

Determination of Vapour-pressure by Air-bubbling.

By EDGAR PHILIP PERMAN and JOHN HUGHES DAVIES.

(Communicated by Principal E. H. Griffiths, F.R.S. Received March 8,—Read March 30, 1905.)

It was shown recently by one of us* that the vapour-pressure of water can be determined with a considerable degree of accuracy by bubbling a current of air through water in a thermostat, and estimating the amount of water evaporated by absorbing it in strong sulphuric acid.

The accuracy of the method has since been questioned,† supersaturation being specially suggested as likely to cause error. We have therefore made experiments in order to discover what error (if any) is introduced by supersaturating the air with moisture before it enters the water in the thermostat. The effect of dust in the air and of electrification have also been investigated. In each case the arrangement of the apparatus was as described in the previous paper.

Supersaturation.—Before passing into the flasks in the thermostat, which was maintained at 70°, the air was bubbled through a large wash-bottle containing water at about 85°. The wash-bottle was connected by a short rubber tube with the flasks at 70°. Otherwise the experiment was conducted as already described. The following results were obtained:—

W.	P.	T.	V.	p.	Vapour-pressure.
gramme.	mm.	° C.	litres.	mm.	mm.
0.6757	753.2	286.1	2.005	736.4	234.7
0.6706	749.3	288.1	2.005	730.2	234.8

The numbers obtained in the previous experiments were 234.2, 233.2, 234.5, 235.0, 233.5, and 233.5, while Regnault's number (corrected as described

* 'Roy. Soc. Proc.,' vol. 72, p. 72, 1903.

† 'Journ. Phys. Chem.,' vol. 8, pp. 299 and 313, 1904.

in the former paper) is 234·0. The supersaturation of the air with moisture caused, therefore, no appreciable effect, the air assuming the normal state of saturation on passing through the four flasks in the thermostat. An explanation of the erratic results obtained by Carveth and Fowler* has already been offered by one of us.†

Dust in the Air.—A thick smoke was made by burning pieces of phosphorus near the inlet tube of the apparatus described in the former paper. The smoke was maintained during the whole of the experiment. The result was as follows :—

W.	P.	T.	V.	p.	Vapour-pressure.
gramme.	mm.	° C.	litres.	mm.	mm.
0·3347	751·8	288·9	1·003	732	235·2

Although a little high, the result can hardly be taken to indicate that the fumes of phosphorus pentoxide had any effect on the amount of water carried off. No doubt there was such an effect in the first flask, but the state of the air became normal before it left the last one. The experiment was not repeated owing to its disagreeable character.

Electrification of the Air.—1. The air was made to pass through a large flask in which hydrogen was being rapidly evolved from zinc and dilute sulphuric acid; the air was thus mixed with electrified hydrogen; it was filtered from the acid spray by a plug of cotton-wool. The result was :—

W.	P.	T.	V.	p.	Vapour-pressure.
gramme.	mm.	° C.	litres.	mm.	mm.
0·3395	763·4	283·4	1·002	747·5	234·7

The effect of the electrification was probably limited to the first or first and second flasks, the result obtained again being normal.

2. One terminal of an induction-coil, capable of giving (with the battery power used) a 6-inch spark, was connected with a wire passing into the first (nearest the inlet) flask in the thermostat; the other terminal was connected with the bath, so that the silent discharge passed through the flasks and the air inside. The result was normal.

W.	P.	T.	V.	p.	Vapour-pressure.
gramme.	mm.	° C.	litres.	mm.	mm.
0·3365	763·4	283·8	1·002	747·3	233·6

* *Loc. cit.*

† 'Journ. Phys. Chem.,' vol. 9, p. 36, 1905.

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3. The X-rays from an ordinary focus-tube were allowed to fall on the flasks in the thermostat, and were specially directed on to the last (nearest outlet). A wire from one of the terminals of a Wimshurst machine was passed down the gauge-tube into the last flask, the other terminal being connected with the bath. With this double arrangement it was thought that the air in the last flask must be strongly electrified and produce a fog. It was impossible to see whether there was a fog or not, but the effect on the vapour-pressure was as expected.

W.	P.	T.	V.	<i>p.</i>	Vapour-pressure.
gramme.	mm.	° C.	litres.	mm.	mm.
0·3473	761·9	282·3	1·002	746·7	237·5
0·3473	761·4	282·9	1·002	745·8	238·0

The greatest deviation from the normal value obtained in these experiments—with the exception of the last two—is slightly over 0·5 per cent., which is almost exactly the same as that obtained in the original investigation.

It may safely be concluded, therefore, that no naturally occurring super-saturation, or dust, or electrification of the air would have any appreciable effect on the result.

*On the Observations of Stars made in some British
Stone Circles.—Preliminary Note.*

By Sir NORMAN LOCKYER, K.C.B., F.R.S., LL.D., Sc.D.

(Received March 15,—Read March 30, 1905.)

In continuation of my work in Egypt in 1891, and Mr. Penrose's in Greece in 1892, I have recently endeavoured to see whether there are any traces in Britain of the star observations which I found connected with the worship of the sun at certain times of the year.

A star rising about an hour before the sun was watched in order to determine the time at which it was necessary to begin the preparations of the sacrifice which took place at the sun's rising. I stated that Spica was the star the heliacal rising of which heralded the sun at Thebes on May-day in the temple of Min, 3200 B.C. Sirius was associated with the Summer Solstice at about the same time. The equinoxes were provided for in the same way in Lower Egypt, but they do not concern us now.

Mr. Penrose found the May-day worship continued at Athens on foundations built in 1495 B.C. and 2020 B.C., on which the Hecatompedon and older Erechtheum respectively were subsequently built, the warning star being now no longer Spica, but the cluster of the Pleiades.

It is generally known that Stonehenge is associated with the Solstitial Year. I have recently suggested that it was originally connected with the May Year, but, so far as I know, no inquiry has yet been made to connect star observations with it or with any other of the British Circles.

I have recently obtained clear evidence that some circles in different parts of Britain were related to the May Year, a vegetation year, which we know was general over the whole of Europe in early times, and which still determines the quarter-days in Scotland.

If the Egyptian and Greek practice were continued here, we should expect to find some indications of the star observations utilized at the temple of Min and at the Hecatompedon for the beginning of the May-year.

Following the clue given me in the case of the Egyptian temples, such as Luxor, by successive small changes of the axis necessitated by the change in a star's place due to precession, I looked out for this peculiarity in an examination of many maps and plans of circles.

I have already come across two examples in which the sight line has been

changed in the Egyptian manner. The first is the three circles of the Hurlers, near Liskeard, a plan of which is given in "Prehistoric Stone Monuments of the British Isles: Cornwall," by H. C. Lukis, published by the Society of Antiquaries, who were so good as to furnish me with a copy, and also some *unfolded* plans on which sight lines can be accurately drawn and their azimuths determined. I am anxious to express my obligations to the Council and officers of the Society for the help thus afforded me.

The second is at Stanton Drew, in Somerset, consisting of three circles, two avenues, and at least one outstanding stone. These were most carefully surveyed by Mr. C. E. Dymond some years ago, and he was good enough to send me a copy of his plans and levelling sections.

To investigate these cases as completely as possible without local observations in the first instance, I begged Colonel Johnston, R.E., C.B., the Director-General of the Ordnance Survey, to send me the 25-inch maps of the sites, giving the exact azimuth of the side lines. This he obligingly did, and I have to express my great indebtedness to him.

Of the various sight-lines found, those to which I wish to call attention in the first instance, and which led me to the others, are

Hurlers.		Stanton Drew.	
Lat. 50° 31' N.	Az.	Lat. 51° 10' N.	Az.
S. circle to central circle	N. 12° E.	Great circle to Quoit	N. 17° E.
Central to N. circle	N. 15 E.	S.W. circle to Quoit	N. 20 E.
N. circle to tumulus ...	N. 19 E.		

For the purposes of a preliminary inquiry in anticipation of the necessary local observations with a theodolite, for which I am making arrangements, assuming hills half a degree high, which roughly compensate the refraction correction so that we may use sea-horizon values, we have the following declinations approximately:—

The Hurlers.	Lat. 50° 31'.	Stanton Drew.	Lat. 51° 10'.
	Dec. N. 38½°		Dec. N. 37°
"	38	"	36½
"	37		

I have prepared a diagram showing the declination of the three brightest stars in the northern heavens, having approximately the declinations in question, for the period 0 to 2500 B.C. The calculations for 0 to 2000 B.C. are taken from the tables published by Dr. Danckwörtt, in the 'Proceedings of

the Astronomische Gesellschaft,' and have been completed from 2000 to 2500 B.C. by Dr. Lockyer.

Vega is ruled out as its declination is too high. The remaining stars Capella and Arcturus may have been observed so far as the declinations go. For time limits we have:—

Dec. N.	Capella.	Arcturus.
38½°	500 B.C.	1550 B.C.
36	1050 „	1150 „

The interesting fact must be pointed out that about 1000 B.C. the declination of the two stars was very nearly the same.

Now there is no question as to which of these two remaining stars we have to deal with, for I find by the use of a precessional globe, that for about 1400 B.C. and 800 B.C. the warning stars were as follows for the critical times of the year, *i.e.*, May, August, November, February.

1400 B.C.			800 B.C.		
		Az.			Az.
May.. .. .	Pleiades rising		Pleiades rising		
August ...	Arcturus rising	N. 14° E.	Sirius rising		
November	Capella setting		Betelgeuse setting		
February...	Capella rising	N. 29 E.	Capella rising	N. 21° E.	
		Dec. 34 N.		Dec. 37 N.	

It is quite clear then that we have to deal with Arcturus, and this being so, the approximate dates of the use of the three circles at the Hurlers can be derived. They are:—

	B.C.
Southern circle aligning Arcturus over centre of central circle ...	1600
Central „ „ „ N. circle	1500
Northern „ „ „ tumulus	1300

I have already pointed out that Mr. Penrose found the warning star for May morning at the date of foundation of the Hecatompodon, 1495 B.C., to be the group of the Pleiades. As the foundations of the Hecatompodon were only built some few years after the stones of the central circle of the Hurlers were used, we ought to find traces of the observations of the same May morning stars. We do: there is a stone with amplitude E. 11° N., which, when aligned from the S circle, would have pointed out the rising place of

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the Pleiades about 1600 B.C., the date we have already found from the observations of Arcturus. I regard this as an important confirmation of the time of the use of the temple, all the more as the high situation of the circles, not generally dominated by higher levels for some miles, renders it probable that large corrections for hills will not be required to be made.

The place of sunrise in November is indicated by sight-lines from all three circles (Az. S. $67^{\circ}9$ E.).

There are alignments in connection with the N. circle which suggest the introduction of the solstitial year, but these and some others may wait till local observations have been made before more is said about them.

With regard to Stanton Drew it is clear that we are there also dealing with Arcturus. Mr. Dymond's levels give an idea of the height of the hills, so with the Ordnance map azimuths, read to 1° , the provisional dates of the use of the Great and S.W. Circles are as under :—

	B.C.
Great Circle	1075
S.W. Circle	1260

*Report on an Area of Local Magnetic Disturbance in East
Loch Roag, Lewes, Hebrides.*

By Captain ARTHUR MOSTYN FIELD, Royal Navy.

(Communicated by Rear-Admiral Sir William Wharton, K.C.B., F.R.S. Received
January 24,—Read February 9, 1905.)

Consequent upon a report received in October, 1902, that on passing eastward of Little Bernera Island at the entrance of East Loch Roag, the Northern Lighthouse Commissioners' vessel had observed her compass to be deflected 5° or 6° , an opportunity was taken by H.M.S. "Research" whilst surveying in the neighbourhood to verify the statement.

Steaming slowly over the ground, in a depth of 16 to 18 fathoms, sandy bottom, the deflection was seen to amount to 10° or 11° , and in a direction contrary to that which had hitherto been noticed by vessels passing over areas of magnetic disturbances in various parts of the world.

Beyond a few preliminary observations to ascertain the horizontal deflection of the needle, nothing further could then be done without special instruments. In the following year, however, the hydrographer, Admiral Sir W. J. L. Wharton, K.C.B., F.R.S., directed a more complete examination to be made, for which purpose a heeling error instrument and Lord Kelvin's deflector were supplied. In June, 1903, H.M.S. "Research" accordingly returned to East Loch Roag, and a week was devoted to making observations for variation, vertical force, and horizontal force at 73 stations, the ship being tautly moored at each.

Owing to the area to be examined lying in a position exposed to a heavy swell from the northward, which was constantly experienced, the observations were made under considerable difficulties.

The results are given in tabular form, from which diagrams have been constructed.

The maximum disturbance from the normal was found to be, for vertical force, 0.056 C.G.S. unit in an upward direction, and for variation $11\frac{1}{2}^{\circ}$, the north seeking end of the needle being repelled from the valley line, which lies nearly in the magnetic meridian.

The "Research" being a composite built ship, is subject to induction when placed in a magnetic field; measures of magnetic disturbances independently of the magnetism induced in the ship are, therefore, impracticable. For this

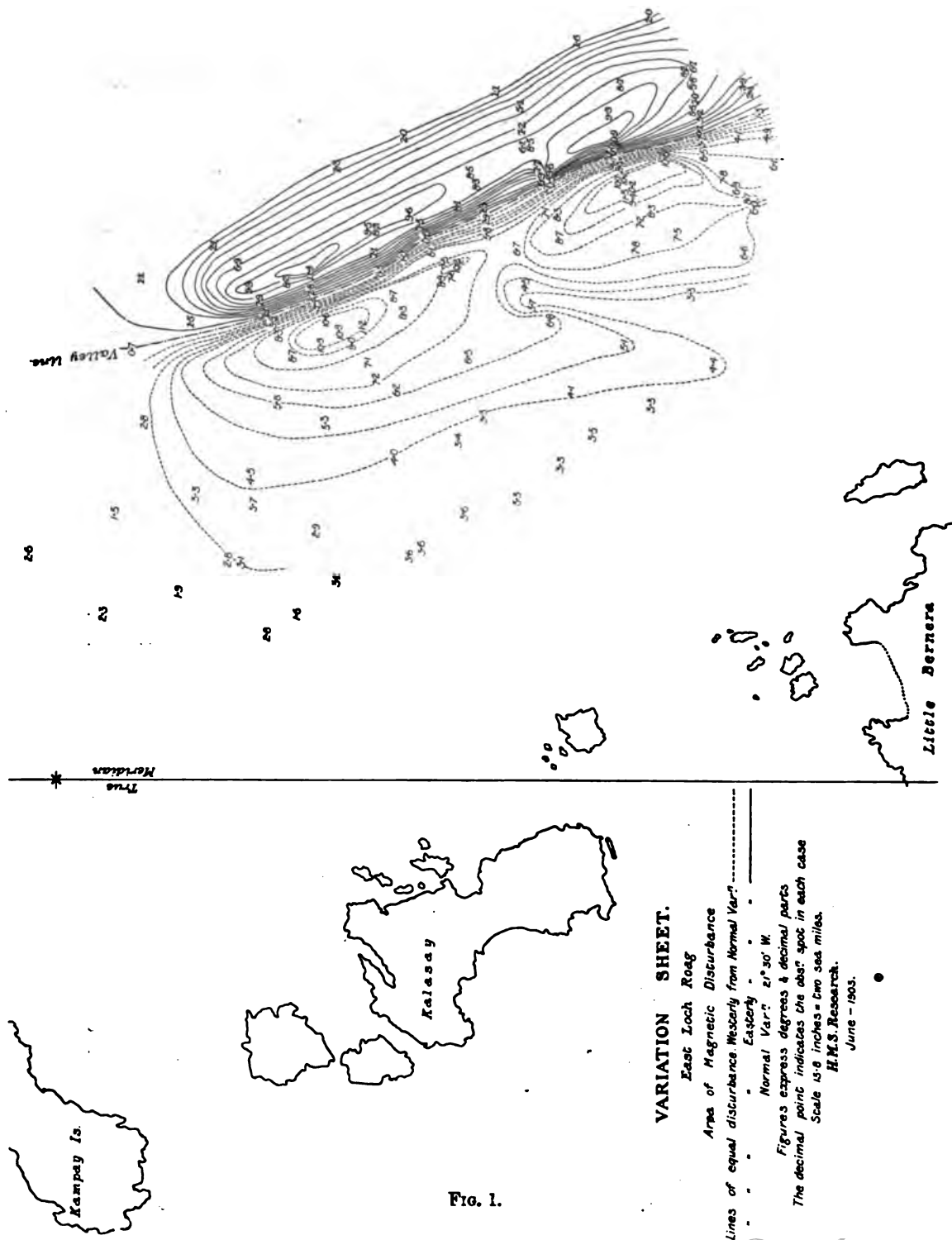


FIG. 1.

reason observations taken on board "Research" can only locate the "magnetic shoal" and measure its extent.

The methods adopted for the survey of this area of magnetic disturbance, so as to obviate as far as possible this limitation, are stated below.

Variation.—The ship was carefully swung for deviation in deep water in the vicinity, but outside the influence of the area of magnetic disturbance.

When in position on the magnetic shoal and tautly moored, the bearing of a distant peak was noted from the standard compass (45 feet abaft the bridge compass and 12 feet above the sea). The ship's position being accurately plotted on the original plotting sheet of Loch Roag (6·9 inches to the sea mile), the true bearing of the distant peak was taken off.

Vertical Force.—The observations for vertical force were obtained on board with the heeling error instrument, at the position of the bridge compass

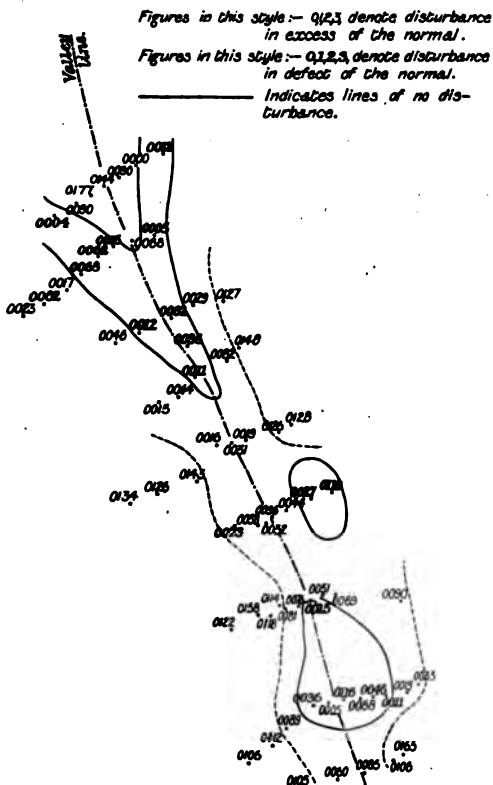


FIG. 2.—Horizontal force. Disturbance from normal in C.G.S. units. Decimal point indicates observation spot in each case. Normal horizontal force in locality, from Professor Thorpe's observations, 0·16507 C.G.S. unit.

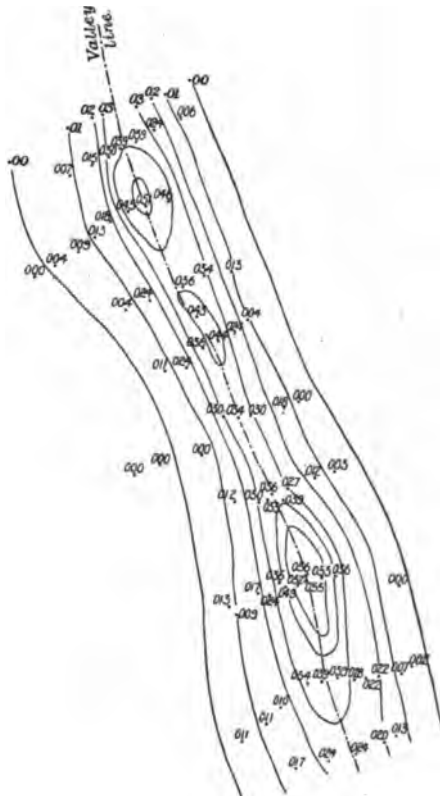


FIG. 3.—Vertical force. Diagram of lines of equal disturbance in C.G.S. units upwards from normal. Normal vertical force in locality, from Professor Thorpe's observations, is 0·451 C.G.S. unit.

16 feet above the sea. The bridge compass and pillar, without its correcting magnets, were subsequently landed at Rücker and Thorpe's Station on Great Bernera Island, and the heeling error instrument was observed to be horizontal with the movable weight set at 38·8 scale divisions.

Horizontal Force.—The observations for horizontal force were obtained on board with the bridge compass (corrected by fore and aft and athwartship magnets) by the aid of Lord Kelvin's deflector set at 12·0 scale divisions, and used as a sine deflector.

After obtaining observations for horizontal force within the area of magnetic disturbance, the ship's head having been noted at each observation, she was then taken into deep water outside the area of disturbance, and the observations repeated with her head in corresponding directions. The bridge compass and pillar, without its correcting magnets, were then landed at Rücker and Thorpe's Station, and with the deflector set at 12·0 scale divisions, the angle of deflection was observed to be 35·15'.

General Remarks.—The anchors were laid out as far apart as possible on either side of the "valley line," and the ship was hauled slowly across with a spring on the cable to keep her head quite steady whilst the observations were being made. A heavy swell caused the ship to roll considerably, making satisfactory observations of the horizontal force especially very difficult to obtain.

The agreement of the "valley line," resulting from the observations for variation and for vertical force, is noticeable.

Placing the (full size) horizontal force sheet over the vertical force sheet, it is observed that the change in value of the horizontal force takes place at the lowest points in the "valley" or line of least vertical force, and shows the repellent force of the magnetism at those lowest points.

The Determination of the Specific Heat of Superheated Steam by Throttling and other Experiments.

By A. H. PEAKE, M.A., A.I.E.E.

(Communicated by Professor Ewing, F.R.S. Received March 16,—Read March 30, 1905.)

In October, 1898, the author commenced experiments, having for their object the determination of the specific heat of superheated steam. At first an attempt was made to obtain this end by measuring the rise in temperature produced in a known quantity of steam by supplying a definite amount of heat in the form of electrical energy, but the experimental difficulties experienced in satisfactorily preventing radiation, in maintaining the rate of flow of steam uniform and in securing a steam supply sufficiently homogeneous and constant as to temperature, proved so great that the attempt on these lines was given up for a time, but returned to later.

Then another method was adopted, that of allowing dry saturated steam to expand without doing external work, and observing the resulting change in temperature. This method had been used in preliminary experiments on this subject by Professor Ewing and Mr. Dunkerley, who found that the specific heat of superheated steam at atmospheric pressure, as deduced by this method from Regnault's values of the "total heat," was not a constant, as had been previously supposed, but increased with temperature.*

While the writer's experiments were in progress, an account of an almost identical research, carried out by Mr. J. H. Grindley, was published in the 'Philosophical Transactions of the Royal Society,' A, vol. 194, pp. 1 to 36. This investigation covered so completely the ground which the author had intended to cover, and the results agreed so well with those obtained up to that time, as to discourage at first any further pursuit of the subject.

However, after careful examination of Mr. Grindley's paper and comparison of results, there appeared to be a somewhat serious source of error common to both his experiments and the author's, and it was decided to proceed with the investigation with the object of obtaining fresh data.

The results finally arrived at appear to amply justify this decision, the source of error, which will be mentioned presently, being gradually reduced and at last effectually eliminated. When this was done the conclusions,

* Note read at the British Association, Toronto, 1897.

while bearing out Mr. Grindley's work in several particulars, differed from it in at least one important feature.

It is well known that if dry saturated steam be allowed to expand without doing external work, and without losing heat, it becomes superheated. The direct object of the experiments was to determine the law connecting the temperature and pressure of superheated steam during this free expansion; then from this law and Regnault's tables of the total heat of saturated steam, the degree of superheat, and the amount of total heat corresponding to this superheat, can be obtained at any particular pressure lower than the initial pressure of the steam, and hence the mean specific heat over that range of superheat, and also the manner in which it varies—if the law be known for various initial pressures—may be calculated. This is, of course, assuming that Regnault's tables of saturated steam are accurate.

Until the throttling experiments were concluded, no doubt was entertained on this point, but it was then seen that a small deviation from the straight-line law laid down by Regnault, connecting total heat and temperature of saturated steam, would have a considerable effect on the calculated specific heat of superheated steam, and the author is now convinced that Regnault's tables are not sufficiently accurate to enable the specific heat to be obtained by this method with any degree of accuracy. In the meantime, however, as Regnault's tables are the only ones available for this purpose, they have been used in the calculations connected with the wire-drawing experiments, so that the final conclusions from these experiments respecting the value of the specific heat of superheated steam must await the correction of these tables.

Let p_1 , t_1 , H_1 , v_1 , and u_1 represent respectively the pressure, temperature, total heat, specific volume, and velocity of dry saturated steam before expansion.

Let p_2 , t_2' , v_2 , and u_2 represent respectively the pressure, temperature, specific volume, and velocity of the steam after being superheated by free expansion.

Also let t_2 and H_2 represent the temperature and total heat of dry saturated steam at pressure p_2 ; let s be the volume of unit mass of water, let J stand for Joule's mechanical equivalent of heat, and let K_p be the mean specific heat of superheated steam at constant pressure p_2 between temperatures t_2 and t_2' .

Then the total energy of unit quantity of steam before expansion is

$$H_1 - \frac{p_1(v_1 - s)}{J} + \frac{u_1^2}{2gJ}.$$

The total energy after being superheated by expansion is

$$H_2 - \frac{p_2(v_2 - s)}{J} + \frac{u_2^2}{2gJ} + K_p(t_2' - t_2),$$

and the heat equivalent of the work done on the steam during the free expansion is $\frac{p_1 v_1 - p_2 v_2}{J}$, for $p_1 v_1$ is the work done on the steam entering the orifice by the boiler steam behind it, and $p_2 v_2$ is the work done by the steam coming from the orifice on the exhaust steam before it.

Now the final energy is equal to the initial energy together with the added energy, that is

$$H_1 + \frac{(p_1 - p_2)s}{J} + \frac{u_1^2 - u_2^2}{2gJ} = H_2 + K_p(t_2' - t_2),$$

so that the total heat is the same both before and after free expansion except for the terms $\frac{(p_1 - p_2)s}{J} + \frac{u_1^2 - u_2^2}{2gJ}$. Both of these quantities are small, and enter as slight correction into the results.

It is, of course, important that the saturated steam before expansion should be quite dry. Failure in this respect was the chief cause of difficulty experienced in the earlier experiments, but when this condition was at last obtained, the experimental results became at once much more simple and satisfactory.

Now in Mr. Grindley's experiments this condition of perfect dryness before expansion was never secured, for after the steam had been allowed to dry in a separator, it was conducted to the orifice disc where the throttling took place along a $\frac{3}{4}$ -inch steam pipe about 1 foot in length, no mention is made of lagging round this pipe, and even if it had been well lagged this would not have entirely prevented radiation, consequently moisture must have been reproduced, the velocity of the steam in the pipe was most probably sufficient to prevent any separating action, and the moisture was carried along.

This defect in the design of his apparatus led him to the erroneous conclusion that what is ordinarily taken to be dry saturated steam, is not really quite dry, but contains a definite amount of moisture, the amount depending upon the temperature.

The principal piece of apparatus used in the author's experiments was virtually a form of throttling calorimeter, specially designed, and gradually improved to avoid, as far as possible, errors due to conduction and radiation, and to reduce corrections dependent upon the kinetic energy of the steam.

After a series of small improvements, the apparatus finally assumed the form shown in part section in fig. 1.

FIG. 1.

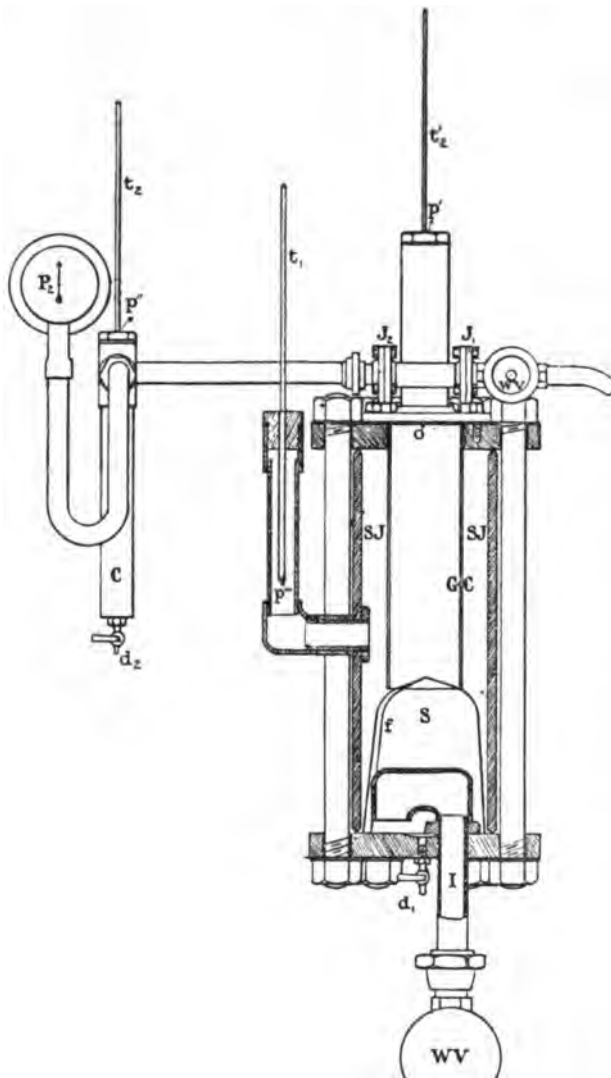


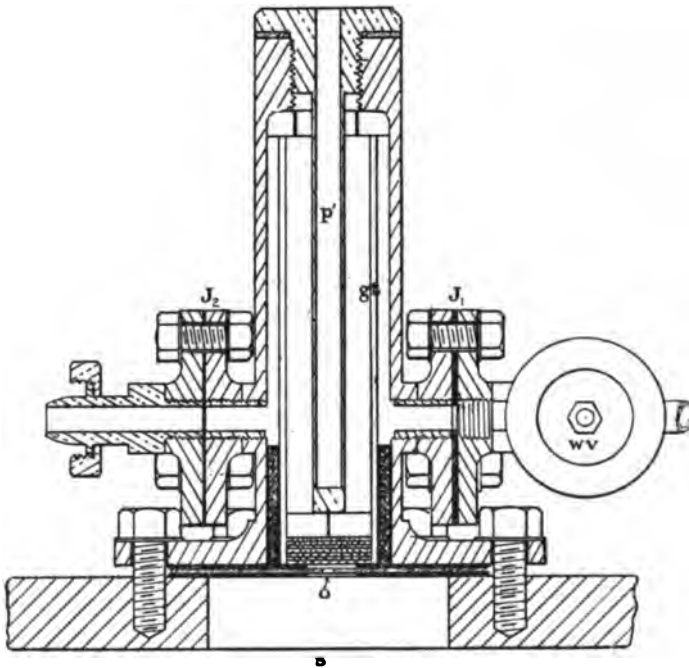
Fig. 2 gives, on a larger scale, a section view of the throttling calorimeter alone.

The steam was taken direct from the crown of a locomotive boiler—not shown in the figure—through a wheel-valve, WV, to a separator, S; it was then allowed to pass through a small orifice, O, in a mica disc, thus being

wire-drawn, or throttled, and consequently superheated. This disc was held down on the top of the separator by a flange and studs, the steam joint being made by placing an asbestos washer on each side of the mica disc; these washers, which only needed a small inside diameter, also materially assisted the mica in the prevention of conduction of heat from the high-pressure steam to the cooler wire-drawn steam.

The now superheated steam coming from the orifice, immediately entered a glass tube, *gt*, and was caused to pass through several layers of fine copper gauze, whose object it was to destroy all eddies in the steam, and convert their kinetic energy into heat energy.

FIG. 2.



Directly after leaving the gauze, the steam came into contact with a thermometer pocket, *p'*, in which was a thermometer for taking the temperature, t_2' , the pocket being concentric with, and inside of, the glass tube; after traversing the length of this tube, the steam passed down an annular space outside it—thus forming, so to speak, its own jacket—and was then allowed to escape into the air through a small wheel-valve, *wv*, which served to regulate the pressure of the superheated steam.

Since the temperature of this valve might be much lower than that of the steam entering it, on account of the throttling which was generally necessary

there, the valve was connected to the apparatus by a heat-insulating joint, J. This joint was made by bolting together two flanges with asbestos packing between, asbestos washers also being placed under the bolt heads and nuts.

The whole of this part of the apparatus from the separator was thoroughly well lagged with felt; this lagging is not shown in the figures.

The pressure reading of the superheated steam was obtained during the more recent experiments in the following manner:—A passage from the side of the apparatus opposite the exhaust valve, *vv*, led through a heat-insulating joint, J₂, similar to the one just described, along an unlagged iron tube about 20 inches in length, to a small chamber, C, containing another thermometer pocket, *p''*, in this chamber the steam was allowed to become saturated—a process which never presented any difficulty—and the water formed was drained out by a cock, *d*₂, at the bottom, a small quantity of steam was allowed to blow through this drain-cock with the water, to ensure that water was not collecting about the thermometer pocket; the temperature, *t*₂, was taken there, and the pressure obtained from Regnault's tables. The flow of steam along the passage was so slight that no appreciable drop in pressure could be attributed to it.

A pressure-gauge, *p*₂, was also fitted; this was not relied on for the true reading, but it was a distinct convenience in working.

Several materials were tried for the orifice discs: glass, boxwood, earthenware, and mica; of these, mica was found to be the most satisfactory, the glass discs invariably cracked, the orifices in the wooden discs closed up, and the discs warped and split; earthenware discs were satisfactory in use, but were not so easily made as mica ones; consequently mica was the material adhered to after the preliminary experiments.

Three sizes of orifice were used, their diameters being respectively $\frac{3}{64}$, $\frac{1}{16}$, and $\frac{3}{32}$ of an inch. The smallest size was used for boiler pressures of 150 lbs. per square inch and upwards, except when the pressure of the throttled steam was required to approach so near to the boiler pressure that the flow became excessively feeble, and a radiation error became apparent, in which case the next size was substituted. For initial pressures between 70 and 110 lbs. per square inch inclusive, the $\frac{1}{16}$ inch orifice was used, and below 70 lbs. pressure, the largest one, $\frac{3}{32}$ inch was used.

No great importance is attached to this, but these sizes were found to be best adapted to those pressures in this particular apparatus. If the orifices were much reduced sufficient steam did not pass to make the radiation loss inappreciable, if they were much increased the blast of steam was inconveniently large, and the gauze might be insufficient in quantity to destroy the eddies.

The separator was constructed out of a piece of 4-inch steam pipe, 12 inches long, the ends were cast-iron flanges, and were bolted together with six $\frac{3}{4}$ -inch bolts; the effective diameter of the separator was, however, considerably reduced by the insertion concentrically of a glass cylinder, GC, a lamp chimney about 8 inches in length and $2\frac{1}{4}$ inches in diameter, which was supported upon a wire frame, *f*, in such a manner that its upper edge was in the same plane as the upper face of the top flange, the annular space round the glass cylinder thus becoming a steam jacket, SJ.

The steam inlet pipe, I, projected through the lower flange, and the direction of the entering steam was changed by means of two elbows, so that it blew against the flange. In this lower flange, also, was fixed the separator drain-cock, *d*₁.

The pressure reading of the steam in the separator was obtained by means of a temperature measurement and Regnault's tables. For this purpose a pipe projecting from the side of the separator contained a third thermometer pocket, *p'''*, to the outside of which the steam had free access, and the pocket contained in turn the thermometer for obtaining temperature, *t*₁; any steam condensing in this pipe drained back into the separator.

Although the pressure in the separator was the same as that in the boiler under ordinary working conditions, yet it was preferred to obtain the pressure from the temperature readings, just as in the similar case previously mentioned, rather than trust to the boiler gauge readings, this method being found to give more accurate results, although the gauges were good ones of their kind, and had been carefully calibrated.

The thermometers used were mercury ones, graduated in divisions of half a degree Centigrade; they had been carefully calibrated previously by indirect comparison in hot oil well stirred with a standard platinum resistance thermometer, originally standardised by the author, and corrections necessary to give the temperature on the air scale were thus obtained to 0.1° C. over the required working range. They were also calibrated in position by blowing saturated steam through the apparatus, the orifice disc first having been removed; the pockets had been made equal in length, and were kept filled with oil just as during ordinary experiments. Although this was a check on the accuracy of the pressure gauges rather than the thermometers, yet the differences between the readings of the various thermometers agreed with those formerly obtained.

It is evident from consideration of the character of the results that a slight difference between the apparent temperatures and the true temperatures on the air scale would have no appreciable effect on the results; it is accuracy of the scale that is of vital importance, hence no correction need be applied for

the effect of the thermometer pockets, since, as has just been shown, if the readings were affected at all they were affected equally.

The temperature readings taken during an experiment were converted into the Fahrenheit scale, as the English system of units was used throughout.

The method of conducting the experiments was as follows:—The boiler pressure was brought to some predetermined value, and maintained constant throughout a complete experiment by continual readings of the temperature of the boiler steam, the slightest observable tendency to change being checked by slight movements of the fire-door or dampers. Steam was then allowed to blow through the apparatus, the separator inlet valve being maintained full open during each experiment, the drain-cocks were opened by a suitable amount, and a few minutes allowed to elapse for the thermometer readings to become settled; as they approached this stage, and for a few minutes afterwards, readings of all three thermometers were taken at intervals of a minute or two. If the temperatures were subject to slight fluctuations, which was often the case, a larger number of readings was taken and the average obtained.

The pressure of the wire-drawn steam was raised step by step by slightly closing the exhaust valve, and the process of taking temperature readings was repeated at each step; by plotting the results with pressures as abscissæ and temperatures of the superheated steam as ordinates, a "cooling curve" could be drawn over which the total heat remained constant except for the very slight corrections before mentioned.

By repeating the experiments with various boiler pressures, a series of "cooling curves" or "constant total heat curves" graphically representing the law sought, was obtained.

Whenever commencing an experiment, if the apparatus was at all wet, it was necessary to allow steam to blow through it for a long time, 10 or 15 minutes, to completely dry that part which was to contain only superheated steam, for it was found that even when the superheat was as much as 50° C., a considerable time was necessary for this purpose, as was evinced by the slow rise in the thermometer reading. It was also necessary to be careful not to raise the pressure of the superheated steam too rapidly or by too great steps, especially when the amount of throttling was not very great, as the heat capacity of the apparatus might be sufficient to cause condensation to take place, and the progress of the experiment be considerably delayed in consequence.

The steam was obtained from locomotive boilers; in the earlier experiments one working up to a pressure of 80 lbs. per square inch was used, but later

the apparatus was connected to the crown of a somewhat larger boiler—rated at 10 horse-power—working up to 200 lbs. per square inch, with which, owing to its capacity, it was much easier to maintain the steam pressure constant.

The boilers were sometimes filled with soft water, sometimes with hard water, either by means of an injector or a pump, but no difference in the results was ever traced to these changes. On getting up steam, the cocks of the water level gauges were left open for some time in order to get rid of air from the steam space. It was impossible to maintain the boiler pressure constant if steam was being taken from the boiler in any quantity for any other purpose, or when the boiler was being filled, so that experiments were only carried out when steam was not wanted elsewhere, and between boiler fillings. One filling often sufficed for two complete experiments.

With a short well lagged connecting stem between the boiler crown and the apparatus—about 9 inches of $\frac{3}{4}$ -inch steam pipe and valve—the results, which agreed fairly well with those published by Mr. Grindley, were obtained, though the fall of temperature before the gaseous condition was reached, was not quite so great. This was before the separator was constructed.

The following brief account of alterations made at various times gives some idea of how the apparatus was gradually improved, and how the “cooling curves” or “constant total heat curves” obtained were thereby raised in greater or less steps until no part lay on the saturation curve, i.e., the curve connecting temperature and pressure of saturated steam.

The length of connecting steam pipe on the low-pressure boiler was reduced until the lower flange of the apparatus—which was afterwards replaced by the separator and is, therefore, not shown in the figures—was as close as possible to the boiler crown, the valves between the apparatus and the boiler being removed. This was, of course, inconvenient, since no change could be made in the apparatus except when the boiler was cold, but the results thus obtained were only lacking in that they covered so small a range.

On the high-pressure boiler it was impracticable so to shorten the connecting pipe; it was, however, made as short as possible, but it was then found that the removal of the steam valve allowed steam to pass wetter than before, showing that the valve must have been acting to some extent as a baffle, causing separation of moisture.

Until these changes were tried it was by no means realised how much the results might be vitiated by quite a short length of well lagged connecting stem.

This fact explained to a large extent the cause of the difficulties met with earlier, and has also an important bearing on the use of throttling

calorimeters generally, since in most cases wetness must be produced from this cause in the instruments themselves, before throttling takes place.

The separator was then constructed and placed on the high-pressure boiler, and the calorimeter placed directly on its crown. Up to this time the steam pressure was read from a test gauge fitted on the boiler, but afterwards it was derived from a temperature reading as previously described.

The glass cylinder inside the separator was also found to be an improvement; this was most probably due to the fact that the separator being of massive construction and unlagged, condensed a large amount of steam, and that portion of the water thus formed on the upper flange rained into the drying steam, unless prevented by the glass cylinder.

The wire gauze just above the orifice was put in the apparatus on first constructing it, but having on one occasion been accidentally omitted, it was found that its absence might cause under the most unfavourable conditions as much as 7° C. fall in temperature as measured by the thermometer, although the higher parts of the thermometer pocket were at a much higher temperature.

This was, no doubt, accounted for by the fact that the full strength of the steam jet from the orifice impinged directly on the base of the pocket, but a little further on the velocity had naturally died out to a great extent.

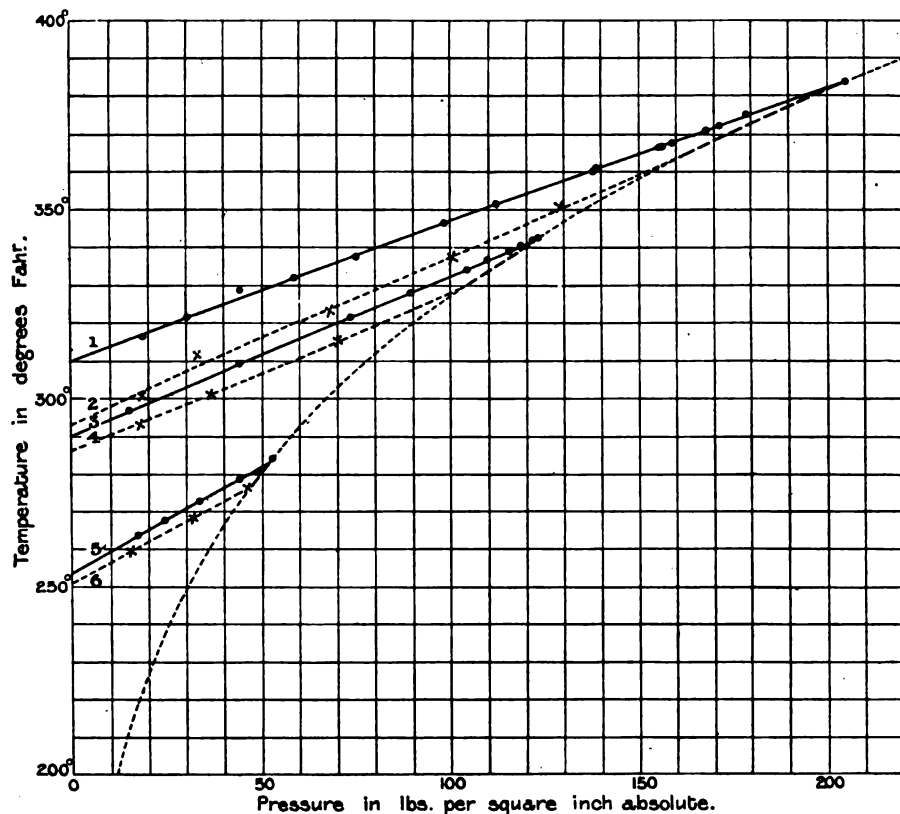
The heat-insulating steam joints, made by means of asbestos washers, which were inserted between that part of the apparatus containing the superheated steam and the colder leading away pipes, formed the last improvement made in the construction of the apparatus.

Fig. 3 gives cooling curves obtained at various stages during the experiments. Curves 1 and 2 show the sum of the errors caused by absence of gauze and radiation loss from a short length of well lagged connecting stem—about 5 inches; 1 was obtained using the separator and gauze, 2 was obtained before the separator was added, and without gauze in the apparatus; in each case the boiler pressure was 190 lbs. per square inch.

Curves 3 and 4 were both obtained with boiler pressure 109; Curves 5 and 6 both with boiler pressure 40 lbs. per square inch. 3 and 5 were obtained with the throttling calorimeter on the crown of the separator, whereas 4 and 6 were obtained without the separator, and show the vitiating effect due entirely to having a connecting steam pipe between the dry steam supply and the orifice, although this pipe was short and well lagged.

The apparatus having now been perfected as far as possible, a complete

FIG. 3.



new series of experiments was carried out, the corrected results of which are given in Table I. The cooling curves obtained by plotting these results are shown in fig. 4.

Before proceeding to the discussion of the curves it will be well to notice the probable and possible corrections. Experiments were made to furnish the necessary data for the calculation of the correction due to the energy of motion of the steam. The quantity of steam passing per minute under the various conditions existing during the experiments was determined by condensing all the steam passed during two or three minutes, and weighing the water thus formed. This quantity did not diminish appreciably until the pressure of the wire-drawn steam was about half that of the boiler steam, but as the pressure of the wire-drawn steam was still further increased, the quantity steadily diminished.

The maximum flow was 0.35 lb. per minute. This occurred with each of the three orifice discs under the maximum boiler pressure to which each was subjected, when the low-pressure side of the disc was atmospheric.

The area of the steam passage by the thermometer pocket was 0.32 square inch.

Assuming the maximum specific volume of steam met with in the course of the experiments—namely at 320° F. and at atmospheric pressure—to be 30, the heat-equivalent of the kinetic energy of the steam, at the point where the temperature of the throttled steam was taken, never exceeded 0.15 heat unit under the most unfavourable conditions experienced, if the eddies in the steam were overcome in a reasonably satisfactory manner by the use of the gauze, and this correction always falls off rapidly as the pressure of the wire-drawn steam is increased, since the specific volume is thereby diminished.

The kinetic energy of the steam on the high-pressure side of the disc is of a much inferior order and may be totally neglected.

Conduction and radiation were combated by the special design of the apparatus, and the sum of all possible errors, due to causes just enumerated, was shown to be constant and therefore most probably inappreciable, by the fact that similar curves were obtained by the use of orifices of different sizes, which of course allowed different quantities of steam to pass, thus changing the relative importance of the various errors. For examples of this see curves A and B, fig. 4. In each of these, different parts of the curves were obtained by different sized orifices (see table), but the overlapping parts coincide.

The change of total heat during free expansion due to the neglecting of the energy existing in the water at 32° F. in the estimation of the total heat, though slight, is perfectly definite, and corrections have been made accordingly before proceeding to calculation of the specific heat. Since this correction $s(p_1 - p_2)/J$ is to be expressed in British thermal units, $s(p_1 - p_2)$ must of course be in foot-lbs., therefore p_1 and p_2 must be the pressures in lbs. per square foot, and s must be 0.016, the volume of 1 lb. of water in cubic feet.

On examination of the set of curves in fig. 4 it is seen that they are practically straight lines, not quite parallel, but becoming slightly more horizontal with higher initial pressures.

However, it appears that if steam ever exists as a perfect gas, it is only at temperatures completely outside the range of these experiments, for the constant total heat curves would then be horizontal.

Although no pressures below that of the atmosphere were ever used in the experiments, yet the curves have been produced to the line of zero pressure, as there is no reason to suppose that the character of the curves suddenly changes in this short length, in fact it was proved by Mr. Grindley's

Table I.

Curve.	Pressure on boiler gauge.	Temperatures of steam.			Pressure from Regnault's tables. P_2	Diameter of orifice in inches.
		Before expansion. t_1 .	After expansion. t_2 .	Re-saturated. t_3 .		
A	191	383.5	°	331.4	250.9	30.3
				316.6	224.4	18.7
				328.8	272.8	43.9
				333.1	290.8	58.4
				337.8	307.4	75.0
				347.0	326.5	96.5
				351.3	335.8	111.9
				360.5	351.7	137.9
				367.0	361.8	156.8
A	191	383.5		315.5	214.9	15.6
				321.6	248.0	28.8
				327.2	273.0	44.0
				332.8	292.1	59.6
				338.3	306.3	73.8
				349.3	330.6	104.2
A	190	383.5		361.2	352.8	138.3
				366.8	361.0	155.3
				367.9	362.8	159.0
				371.3	367.3	167.9
				372.4	369.1	171.7
				375.1	372.4	178.8
B	150	365.0		308.5	220.6	17.4
				313.7	245.3	27.5
				318.9	270.1	42.0
				326.1	294.1	61.5
				332.6	309.9	77.8
				338.4	323.1	94.0
				343.8	333.5	108.4
				350.8	345.2	126.7
B	150	365.0		333.6	311.2	79.3
				346.5	337.2	113.8
				350.3	343.4	123.8
				353.8	349.4	133.9
				355.1	351.3	137.2
B	150	365.0		350.3	343.9	124.6
				351.9	346.5	128.9
				353.7	349.3	133.7
				354.9	351.3	137.2
				357.4	354.9	143.7
				363.7	363.7	159.3
C	109	342.8		297.0	212.0	14.7
				321.8	306.1	73.6
				328.1	318.4	89.2
				334.5	330.4	104.2
				337.1	334.2	109.5
				339.3	338.0	115.2
				340.9	340.0	118.3
				349.0	372.8	43.9
				342.1	342.1	121.7

Table I—continued.

Curve.	Pressure on boiler gauge.	Temperatures of steam.			Pressure from Regnault's tables. p_2	Diameter of orifice in inches.
		Before expansion. t_1	After expansion. t_2'	Re-saturated. t_2		
D	71	315.1	281.9	215.4	15.7	1/16
			285.9	224.1	22.4	
			291.5	257.0	33.7	
			292.1	258.3	34.5	
			296.4	271.2	42.8	
			301.6	286.0	54.2	
			306.8	296.2	63.5	
			310.4	306.5	74.0	
E	40	284.1	312.8	311.4	79.6	3/32
			263.2	218.1	16.6	
			267.4	227.9	24.1	
			272.0	255.4	32.8	
			278.7	272.9	44.0	
			280.2	279.5	48.9	
F	20	256.5	284.0	284.0	52.6	3/32
			244.6	214.9	15.6	
			250.5	239.7	24.9	
			253.5	249.3	29.5	
			256.6	256.5	33.4	

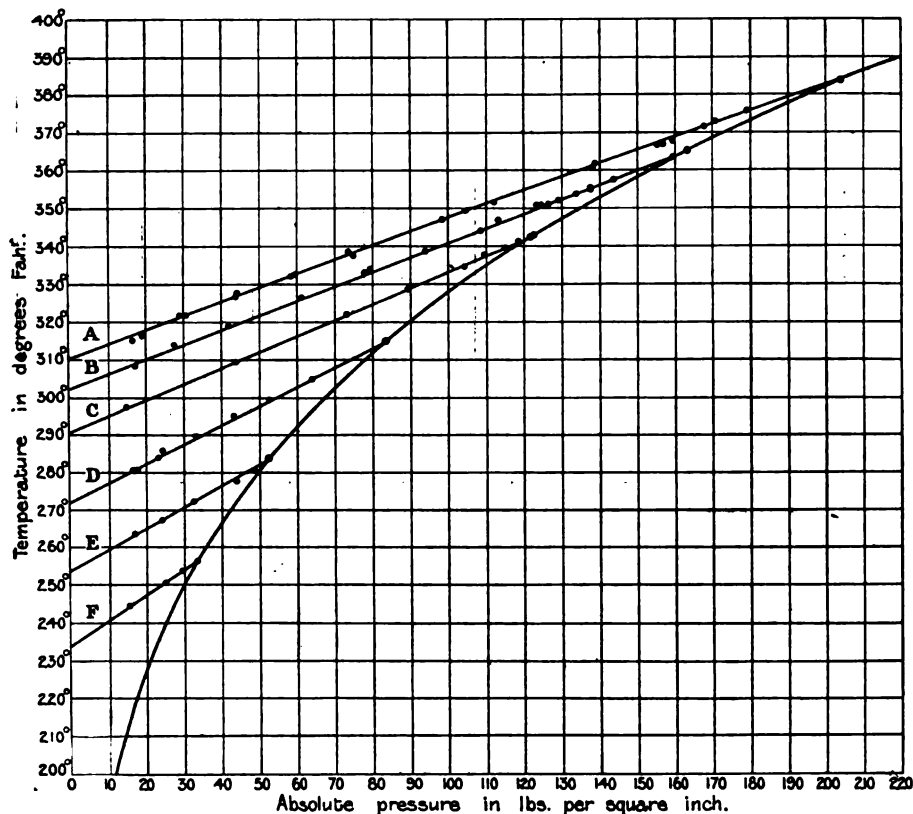
experiments that the character does not so change when the steam is throttled down to a pressure of 2 or 3 lbs. per square inch absolute.

The maximum boiler pressure available was, as previously stated, 200 lbs. per square inch; however, if a pressure of 336 lbs. absolute had been available, which is the maximum value given in Regnault's tables, and is therefore the limiting pressure by methods based on his figures, the upper limit of fig. 4 would only have been altered by a very small amount, since the additional total heat of saturated steam corresponding to this increase of pressure, is only 12.5 units.

From fig. 4, Table II has been constructed, showing the connection between total heat according to Regnault—corrected by the slight change in the total heat that takes place during free expansion as explained earlier—and temperature at constant pressure for various pressures, and the results contained in this table are represented graphically in fig. 5.

The slope of the curves in fig. 5 gives, then, the specific heat of steam at constant pressure, according to the author's experiments, based on Regnault's tables of the total heat of saturated steam. It will be noticed that where two or more curves cross the same ordinate, the slope is about the same for

FIG. 4.



each, therefore, as far as can be judged from these experiments, the specific heat of superheated steam is independent of pressure.

Table III gives the relation between specific heat and temperature as derived from the curves in fig. 5, and fig. 6 shows this relation graphically, ordinates representing specific heat, and abscissæ representing temperatures.

FIG. 5.

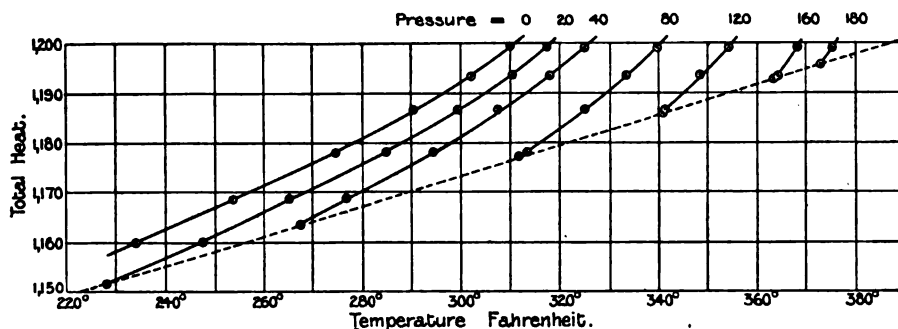


Table II.

Pressure = 0.		Pressure = 20.		Pressure = 40.		Pressure = 80.	
H.	t.	H.	t.	H.	t.	H.	t.
1199·3	310·0	1199·3	317·8	1199·4	325·1	1199·3	339·8
1193·6	302·3	1193·6	310·4	1193·6	318·0	1193·5	333·3
1186·8	290·5	1186·8	299·0	1186·7	307·4	1186·8	324·6
1178·1	275·0	1178·1	285·0	1178·0	294·2	1177·9	313·4
1168·6	253·8	1168·6	265·0	1168·6	276·6	1177·0	311·8
1160·1	234·1	1160·1	247·5	1163·4	267·1		
		1151·5	227·9				

Pressure = 120.		Pressure = 160.		Pressure = 180.	
H.	t.	H.	t.	H.	t.
1199·1	354·2	1199·0	368·3	1198·9	375·2
1193·4	348·5	1193·3	364·2	1195·7	373·0
1186·5	341·5	1192·3	363·4		
1186·0	341·0				

FIG. 6.

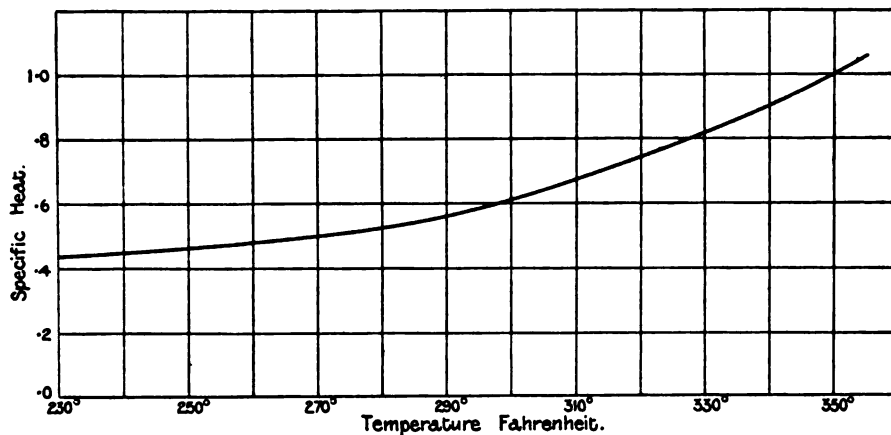


Table III also contains, for comparison's sake, the values of the specific heat given by Grindley, whose results, also, are dependent on Regnault's tables. It will be at once apparent, on comparing the results given in Table III, that they agree fairly well over that part of the range common to both, showing that a considerable error in the cooling curves does not necessarily vitiate, to any great extent, the value of the final deductions with regard to the value of the specific heat.

Table III.

Present experiments.		Grindley's results.	
Temperature.	Specific heat.* (K_p).	Temperatures between which mean specific heat is taken.	Mean specific heat.* (K_p).
230	0.43	.	.
240	0.44	230.7—246.5	0.4317
260	0.47	246.5—260.8	0.4778
280	0.53	260.8—269.7	0.5152
300	0.61	269.7—295.0	0.5646
320	0.75	295.0—311.5	0.6482
340	0.91		
350	1.00		

The apparent rapid increase of specific heat with temperature to values far beyond any obtained by any other experiments known to the author, led him to suspect the accuracy of Regnault's tables, and caused him to return to the direct heating method as mentioned earlier, with the hope, also, of getting results for higher temperatures than were possible by the throttling experiments.

The existing apparatus was altered as follows, so as to be able to be used in the new experiments. The orifice disc, and most of the gauze above it, were removed; the tube which led to pressure gauge, p_2 , and to the thermometer which gave the corresponding saturation temperature, was also taken away, and the broken joint plugged up.

The steam, instead of blowing into the atmosphere, was led through a surface condenser, consisting of one long, straight tube, inside and concentric with a larger one, through which cold water circulated, and then into one or two glass flasks, also immersed in cold, circulating water; these flasks could be removed easily from time to time, and weighed, and by weighing one of the flasks while the other was filling, the experiment could be made quite continuous during a time sufficient to collect several flasks full of condensed steam.

The straight tube surface condenser cooled the steam sufficiently to allow

* As deduced on the assumption that Regnault's values of the total heat of saturated steam may be accepted as correct.

the flask to be open to the atmosphere without losing steam by leakage, and hence the condenser was always at atmospheric pressure.

The electric heater was made of No. 24 German-silver wire, wound in coils on small glass tubes, the whole being enclosed in a glass tube 1 inch in diameter and 8 inches long; this tube was placed in the centre of the separator, with its upper edge placed against the asbestos washer, where the orifice disc was originally, so that all the steam passing through the apparatus was compelled to pass over the heater. Before, however, the steam could reach the heater from the separator, it was compelled to pass along two concentric passages, which enclosed the tube containing the heater; by this means it was sought to avoid loss of heat by radiation, the steam coming in towards the heater taking with it the heat which was being radiated to the walls of the passages.

The electric current was led to the heater by two stout brass conductors, which passed through the cast-iron base of the separator, and were insulated therefrom by conical slate plugs let into the iron.

The room available for the heater was unfortunately very small, and the wires were in consequence crowded rather closely together, with the result that in one or two instances, when very hot, failure of the apparatus was caused through short circuits.

The input of electrical energy was measured by means of an ammeter and voltmeter, which were calibrated from time to time on a Crompton potentiometer, and the necessary corrections applied in the calculations.

Mercury thermometers were used as before, reading in degrees Centigrade, but reading to higher temperatures, the corrections at these higher temperatures were found to be surprisingly large; the calibration of the thermometers was a matter of considerable difficulty, they were, however, compared with the standard platinum resistance thermometer mentioned earlier. The comparison was made by immersing the thermometers in cylinder oil, heated by a gas flame and stirred by means of a small motor. This method of comparing thermometers in a well-stirred fluid appeared to be the only satisfactory one among many attempts.

It was found impossible to entirely eliminate radiation losses, and after a few preliminary experiments, the method of procedure was to aim at keeping steady the temperatures of the steam before and after heating, and then as quickly as possible to obtain the connection between grammes of steam passing per minute and watts required to maintain this constant difference of temperature, this being done for several rates of flow of steam differing over a considerable range. The connection between grammes per minute passing and the input of electrical energy in watts, for a definite temperature

rise, was then plotted on squared paper; the points thus obtained would lie on a straight line, which, however, did not pass through the origin, but cut the axis of watts at a height corresponding to the radiation loss expressed in watts. From the slope of the curve, or the increase of watts necessary to maintain a given temperature rise when a definite increase in the flow of steam took place, the specific heat of superheated steam at constant pressure could be calculated by the formula

$$K_p = \frac{\text{Electrical input in watts} \times 0.236}{\text{Grammes of steam passing per second} \times \text{temp. rise } ^\circ \text{C}}$$

In practice it was found impossible to so adjust the watts that the temperature rise was constant throughout any one series of experiments on account of the time necessary; the watts were rapidly adjusted however to produce a rise as near as possible to the one aimed at, and then the watts were corrected for this particular temperature rise on the assumption that for such slight differences in temperature the rise was directly proportional to the watts. Even then a considerable time was required for all the conditions to become steady before every point obtained.

The difficulty of keeping all the conditions constant during the long time necessary for a complete set of points was always considerable, many of the experiments being spoilt through failure of one condition.

Table IV gives the data obtained in a few characteristic experiments, and

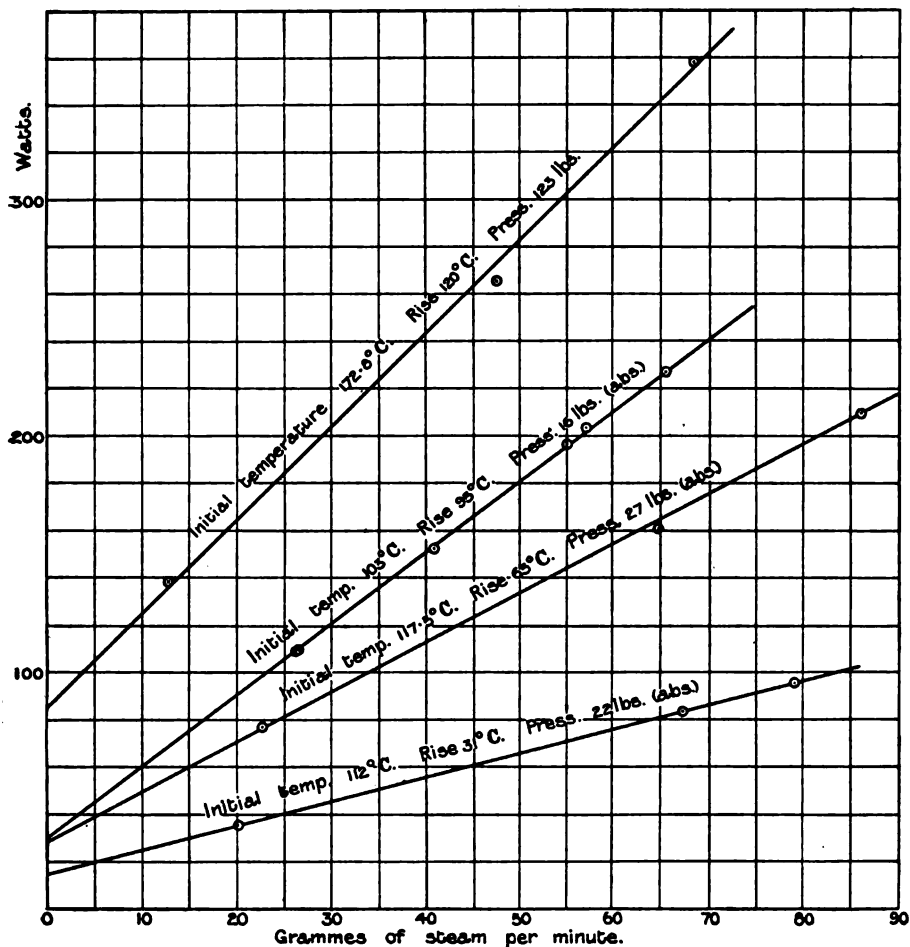
Table IV.

Mean initial temperature.	Mean final temperature.	Rise in $^\circ \text{C}$.	Watts.	Watts for rise of—	Grammes of steam per min.	K_p .
112.8	144.2	31.4	34.8	(31°) 34.4	20.1	} 0.473
111.6	142.4	30.8	33.1	33.7	67.2	
111.7	142.6	30.9	95.1	95.4	79.1	
117.5	182.6	65.1	76.6	(65°) 76.5	22.9	} 0.452
117.6	182.7	65.1	160.4	160.2	64.7	
117.4	183.1	65.7	211.5	209.3	86.0	
102.7	196.3	93.6	106.5	(95°) 106.1	26.4	} 0.458
102.7	197.8	95.1	109.5	109.4	26.6	
102.7	198.6	95.9	153.5	152.1	40.9	
102.6	199.5	96.9	200.5	196.5	55.1	
102.7	196.3	93.6	200.5	203.5	57.1	
102.7	200.7	98.0	235.0	227.8	65.4	
173.0	289.6	116.6	134.3	(120°) 138.3	13.0	} 0.459
172.9	293.7	120.8	267.0	265.5	47.3	
172.5	297.0	124.5	372.0	358.2	68.3	

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the resulting value of the specific heat thus obtained. The connection between watts and flow for a definite rise in temperature is also shown graphically in fig. 7 for the same experiments.

FIG. 7.



Numerous experiments were carried out, but the results varied too much amongst themselves to allow any conclusions to be drawn as to the manner in which the specific heat may vary with pressure or temperature, except that any such variation must be small, and by no means of the order indicated by the results of the throttling experiments based on Regnault's tables.

The mean of all the results gave $K_p = 0.43$, but the author believes that

the value 0.46 is more accurate, this being the average of the values obtained in the most satisfactory experiments.

The experiments were all carried out in the Engineering Laboratory of Cambridge University, and the author is indebted to Professor Ewing, F.R.S., for much kindly advice and encouragement given during the course of the research.

On the Distribution of Velocity in a Viscous Fluid over the Cross-Section of a Pipe, and on the Action at the Critical Velocity.

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1. *Introduction.*—An expression for the velocity at which stream-line motion breaks down in cylindrical pipes has been obtained by Osborne Reynolds,* and together with many others he has measured the fall of pressure occurring in different lengths. Lord Kelvin,† Lord Rayleigh,‡ and Reynolds§ have investigated the stability of different kinds of flow for viscous and non-viscous fluids, but how nearly the theoretical conditions of velocity distribution actually occur has not hitherto formed the subject of research. Experiments have often been made on the variation of mean linear velocities in the eddying state, but when the motion is irrotational, these are too low to admit of accurate measurement by any method so far employed.

The objects of the present paper are to determine these velocities, to investigate the change which takes place at the critical velocity, and to find the relation between the velocity and the pressure to which it gives rise in a "Pitot" gauge of the form used.

The research has become possible chiefly through the aid of an exceedingly delicate pressure gauge recently designed by my colleagues Professor A. P. Chattock and Mr. J. D. Fry. I am indebted to both these gentlemen for much valuable advice.

* 'Phil. Trans.,' 1883, Part III, p. 935.

† 'Phil. Mag.,' August, 1887.

‡ 'Phil. Mag.,' July, 1892, etc.

§ 'Phil. Trans.,' A, 1896, vol. 186, p. 123.

Osborne Reynolds has shown that in parallel channels there are two limits to stream-line flow. The lower one is the velocity at which motion, originally eddying, will, when left to itself, settle down into stream-line motion, and the upper limit is that at which the motion of a fluid, originally at rest, traversing a pipe in an unstable stream-line condition, suddenly breaks down into the eddying or turbulent state.

The variation of the lower limit with change of temperature has been further investigated by Coker and Clement,* and similarly that of the upper limit by Barnes and Coker.† The present paper deals with the lower limit of stream-line flow, and the term "critical velocity" is used in that sense throughout.

2. *Description of the Apparatus.*—In an earlier apparatus the pipe was about 2.5 cm. in diameter and the Pitot tube 20 cm. long. There was danger of the Pitot tube bending, the velocity distribution was not symmetrical, and the temperature effects were considerable.

In the new apparatus the pipe was of glass, 5.088 cm. in diameter. It was arranged with a bell-mouth in the entrance chamber, so that the water should enter under circumstances conducing to steadiness of flow, and by means of a fine tube a stream of colour could be admitted to indicate the nature of the motion. The water was supplied from the hydraulic installation at University College, Bristol, and there was no other discharge from the mains while the experiments were in progress.

The Pitot and static head tubes are shown in fig. 1, D being a brass pipe in continuation of A. To insure accuracy in the motion of the Pitot tube, *p*, it was carried by a rigid rectangular framework composed of a tube *qq*, a rod *rr*, and two cross-pieces E and F. The guides in which this frame slides are two short tubes G and H and the longer one KL, and to these are attached the cross-piece M and scale S.

Thus, by turning the screw R, the Pitot may be traversed across the pipe, its exact position being indicated by the reading on the scale opposite an index on F.

The static head tube is at Q, a hole being drilled in the side of the glass pipe. A connection to *qq* would, therefore, give the pressure due to the velocity and static head combined, whilst one to Q would give the static head only.

The two passages from the Pitot tube pass to one end of a reversing device, the other end of which is in communication with the static head tube. The two sides of this circuit are connected to the limbs of the pressure

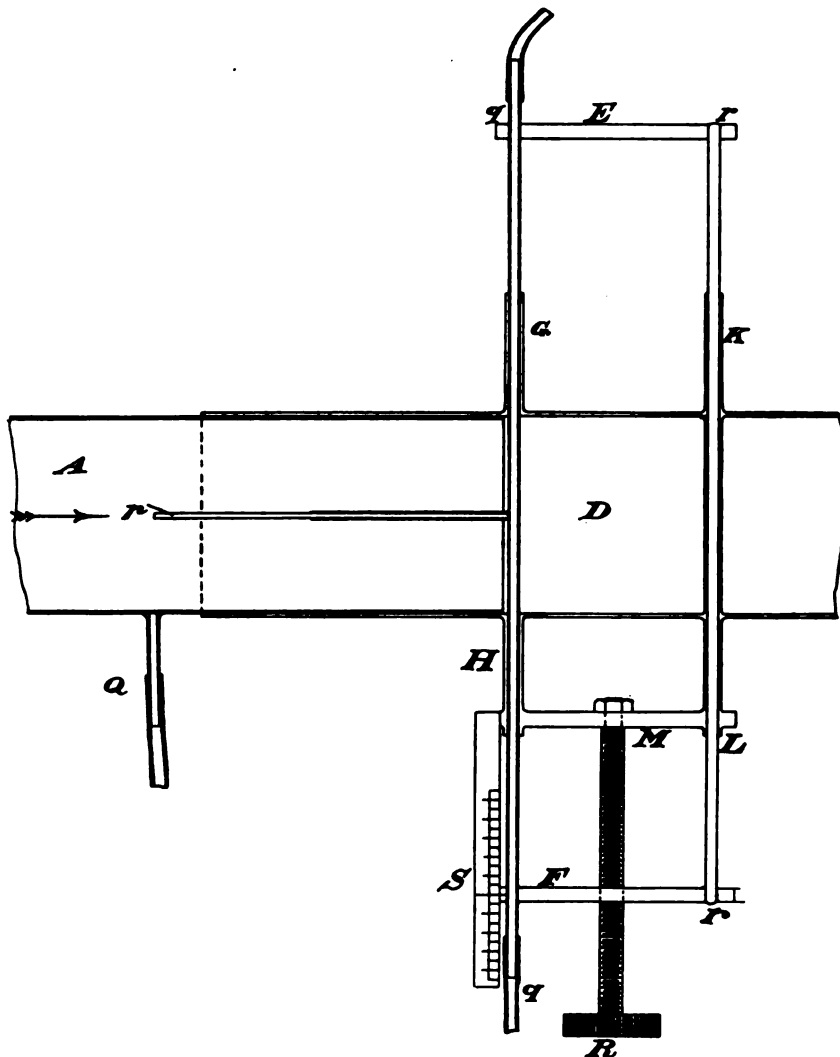
* 'Phil. Trans.,' A, vol. 201, pp. 45—61.

† 'Roy. Soc. Proc.,' vol. 74, p. 341.

gauge. By this means (1) the static head can be brought to one side of the gauge and the Pitot tube to the other; (2) the arrangement may be reversed; or (3) the gauge may be short circuited on itself.

It was found useful to be able to damp the slight oscillations occurring

FIG. 1.



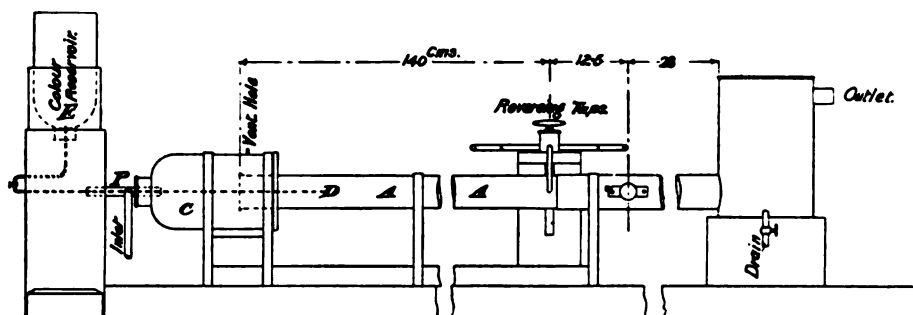
at some velocities in the pressure gauge. For this purpose a small air chamber and two constricted passages were provided. They could be cut out of the circuit, and were only used for verifying previous observations.

Fig. 2 is a general view. It will be seen that the discharge took place

into a tank at the end of the pipe, and from there the water passed to waste by an overflow.

The whole apparatus is carried on a stout timber base, the pipe and its attachments at each end being very carefully centred so as to ensure a maximum and symmetrical flow.

FIG. 2.



3. *Measurement of pressure, discharge, and temperature.*—The pressure gauge is of the Chattock-Fry differential type, and in construction is very similar to that in use at the National Physical Laboratory.* As employed in this research, however, it depended for its action on the difference in density of two liquids.

From fig. 3 it will be seen to consist essentially of a U-tube, of which *bb* are the arms and *aa* the horizontal connection. The two parts of *aa* meet in the chamber *O*, and the fluid pressure is applied at *CC*. The tubes *aa* and the lower portions of *bb* contain carbon-tetra-chloride, whilst the upper portions of *bb* and the chamber *O* are filled with water. A meniscus surface of separation is shown at *s*, and the manipulation of the gauge consists in keeping the surface, viewed through the microscope *M*, absolutely unaltered in position. This is done by turning the graduated disc of the screw, and so tilting the gauge through the small angle necessitated by the variation of pressure difference. There is in this way no motion of the liquids relatively to the glass tubes which contain them, and hence errors due to surface-tension, refraction, or viscosity are entirely avoided.

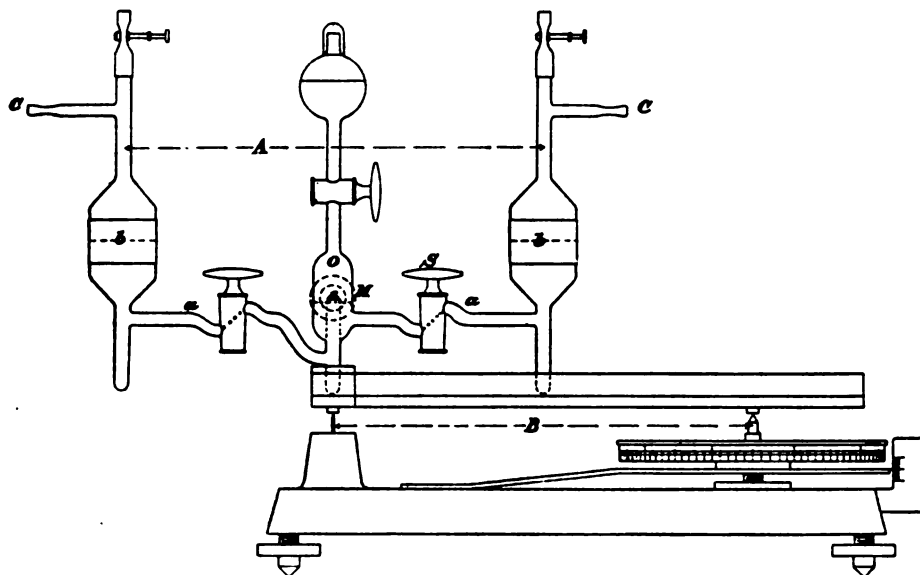
The pitch of the screw was 1 mm., and on the circumference of the disc were 200 divisions. These could be further divided by a vernier, but its use was abandoned as being within the limit of sensitiveness of the meniscus surface and microscope.

* See Stanton, 'Proc. Inst. C.E.,' vol. 156.

A and B being the dimensions shown in fig. 3, and R the reading of the screw, the pressure difference is given by

$$p_1 - p_2 = (\rho' - \rho) g \frac{A}{B} R.$$

FIG. 3.



A/B was found to be 1.038 and $(\rho' - \rho)$ was taken from measurement on a Westphalia Balance to be 0.600 at 17° C.

To obtain the mean velocity of the water, it was necessary to measure the discharge. This was done by collecting the water passing through the apparatus in a given time, and weighing it on a carefully-calibrated spring balance to the nearest 10 grammes. The temperature was obtained by a thermometer placed in the end tank close to the outlet of the pipe.

4. *Method of making the Experiments.*—In determining the velocity distribution, experiments were made with the Pitot tube in various positions, commencing near one side of the pipe and continuing at successive points across the diameter, the water running continuously while a complete series of observations was made. The temperature was noted, and the discharge taken as the mean of six independent measurements.

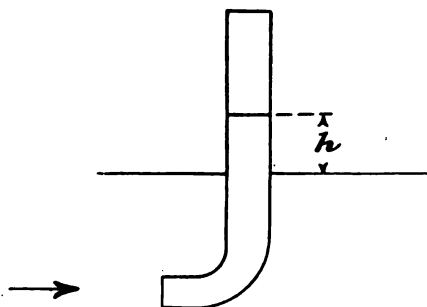
The following was the general system adopted for reading the pressures:—For any position of the Pitot tube, connection with the pressure gauge was made by opening the taps, the gauge was adjusted, and the reading taken. The connections were then reversed, and the reading taken. To eliminate errors due to friction or surface-tension, the observation was then repeated by

closing the tap S, setting the pressure gauge to the previously obtained reading, reversing the connections, and then re-opening S. This was continued until there was no apparent motion of the meniscus surface. The difference between the two readings was then double that due to the velocity of the stream at the point. A check on the accuracy of the gauge was applied during each series of readings. The instrument being adjusted when short-circuited, its zero reading was taken. The pressure due to the velocity was then read on each side of this zero.

In the earlier experiments errors were discovered in this way, and found

to be due to a very slight eccentricity of the point of the screw. Tests were also made for displacement of the surface when no water was flowing, and occasionally a very small correction had to be allowed. This was attributed to slight differences of temperature in the passages leading to the gauge.

FIG. 4.



as in the Bernoulli Theorem, that the flow is steady, and that the velocities of consecutive stream-lines are not widely different, we may treat the fluid immediately at the mouth of the tube as at rest, and apply the theorem as though unimpaired by viscosity.

The pressure p in the stationary fluid is then given by

$$p = \frac{1}{2}\rho v^2,$$

for this is the pressure in the adjoining stream-tube, where the velocity is indefinitely small. The formula requires experimental verification. Since the pressure must be proportional to ρv^2 we may in all cases assume

$$p = \frac{1}{k^2} \cdot \frac{\rho v^2}{2}.$$

If h is the height above that due to the static head, to which the fluid will rise, the velocity of the stream approaching is

$$v = k\sqrt{(2gh)},$$

where k is the Pitot constant to be determined. This may be done by a comparison of the gauge readings with the discharge from the pipe. The total flux Q is

$$2\pi \int_0^a r v dr,$$

5. *Determination of the Pitot Constant.*—If a tube be placed in a stream, as shown in fig. 4, and it be assumed,

where v is the velocity distant r from the centre, and a the radius of the pipe. And, since $v = c\sqrt{(R)}$ where R is the gauge reading and c a constant, we may write

$$Q = 2\pi c \int_0^a r\sqrt{(R)}dr.$$

To determine the integral, curves were plotted having r as abscissæ and $r\sqrt{(R)}$ as ordinates. The areas enclosed by the curves were then calculated by the method of ordinates, and the values obtained used for finding c , and hence the Pitot constant k . An example is given in Table I, in which readings were taken at 19 different points in the diameter of the pipe.

Table I.

r .	2.25.	2.00.	1.75.	1.50.	1.25.	1.00.	0.75.	0.50.	0.25.	0.00.
$\sqrt{(R)} \times 10^2$	4.24	7.07	9.53	11.21	12.08	12.72	12.99	13.26	13.44	13.52
$r\sqrt{(R)} \times 10^2$	9.54	14.84	16.68	16.81	15.10	12.72	9.74	6.63	3.36	0.00

$Q = 59.8$ c.c. per second. $k = 1.06$.

The second line in the table contains the square roots of the means of corresponding readings on each side of the centre. In fig. 5 the $r\sqrt{(R)}$ curve shows the relative flux through different elemental tubes, into which we may suppose the stream to be divided. Its area was obtained from the mean of 83 ordinates. The $\sqrt{(R)}$ curve is proportional to that of velocity distribution. The mean value of k obtained from the six experiments described in the next section is 1.04, and in calculating velocities I have adopted this constant throughout. The number may be compared with those recently found for air, namely, 1.03, by Dr. T. E. Stanton* and 0.974 by Mr. R. Threlfall, F.R.S.†

6. *Velocity Curves for Different Rates of Discharge.*—Experiments were made at six rates of discharge, the curve of distribution of velocity being obtained in each case, and the result checked by comparing the mean velocity from the Pitot readings with that obtained from the actual measurement of the discharge.

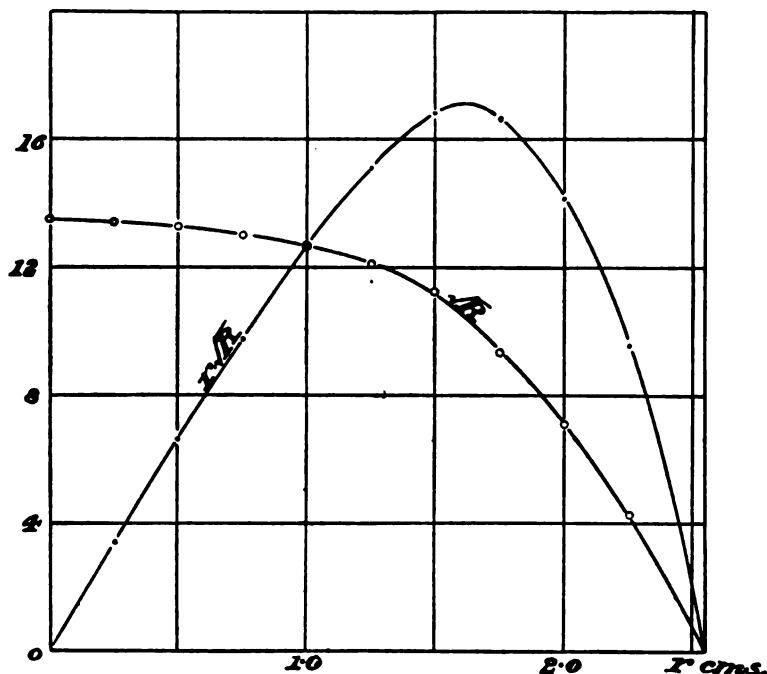
The critical velocity, as determined by the point at which the law of velocity distribution changed, occurred when the mean was about 4 cm. per second (this being, of course, the velocity at which stream-line motion ceased to be the stable flow), and above this there was a decided change in the way in which the velocities increased with an increasing discharge.

* 'Proc. Inst. C.E.,' vol. 156.

† 'Proc. Inst. Mech. Eng.,' 1904.

The observed readings were reduced to velocities as already described, and these are given in Tables II and III. The $r\sqrt{R}$ curves were plotted, and the values of k determined.

FIG. 5.



The temperature varied between 17° and 19° C.

Table II.—Experiments below Critical Velocity.

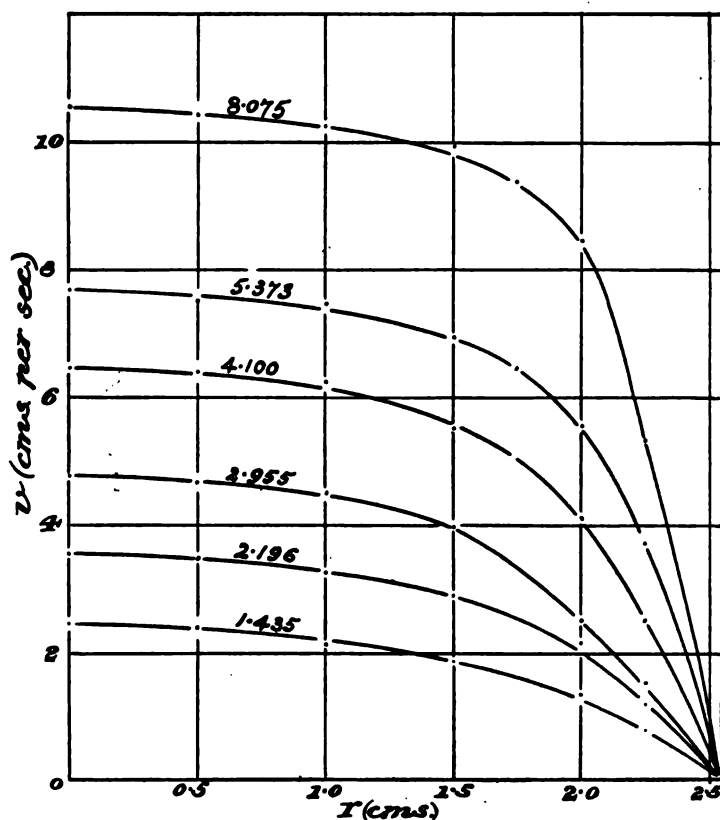
Mean velocity in centimetres per second.	Velocity in centimetres per second.						Value of <i>k</i> .
	Radii in centimetres.						
	0.	0.5.	1.00.	1.50.	2.00.	2.25.	
1.435	2.43	2.39	2.13	1.85	1.33	0.78	1.05
2.196	3.56	3.45	3.22	2.88	2.16	1.17	1.03
2.955	4.77	4.67	4.48	3.96	2.49	1.50	1.05

Table III.—Experiments above Critical Velocity.

Mean velocity in centimetres per second.	Velocity in centimetres per second.							Value of <i>k</i> .
	Radii in centimetres.							
	0.	0.5.	1.00.	1.50.	1.75.	2.00.	2.25.	
4.100	6.43	6.39	6.12	5.50	5.14	4.07	2.48	1.04
5.373	7.67	7.51	7.44	6.93	6.42	5.53	3.70	1.02
8.075	10.57	10.42	10.25	9.94	9.38	8.42	5.30	1.05

The curves in fig. 6 are obtained by plotting the numbers in the last two tables. They show, as ordinates, the actual velocity of the stream at

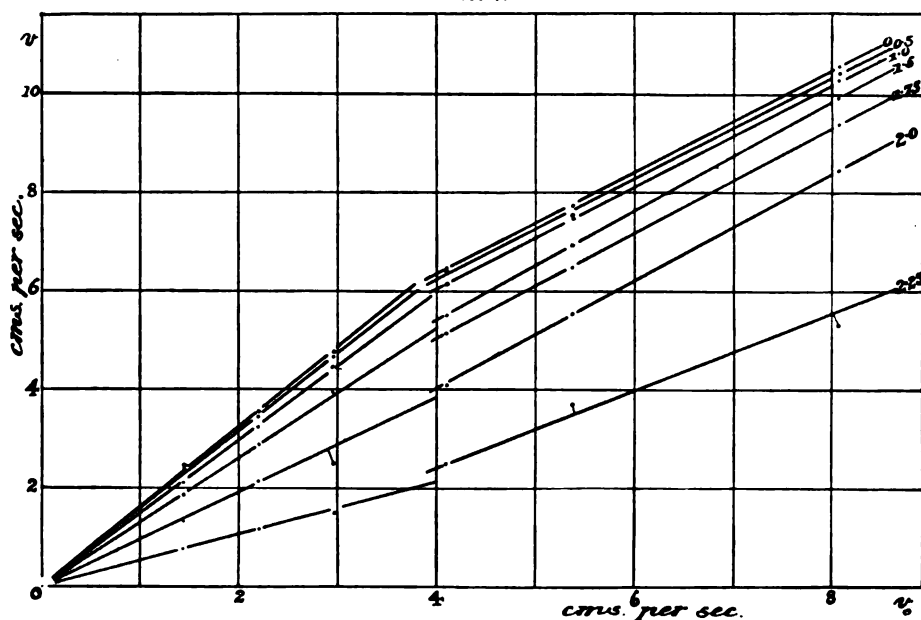
FIG. 6.



different distances from the centre of the pipe, the figures on the curves denoting the mean velocity as calculated from the discharge.

It will be seen that below the critical velocity, the curve approximates to a parabola, and that afterwards there is a gradual change in form in the direction of a uniform velocity in the greater part of the pipe with a sudden fall to zero at the walls. These results are contrary to the frequent statement that, when the conditions of flow change from stream-line to eddying or rotational motion there is an equally sudden change in the law of distribution of linear velocity from the parabolic to nearly uniform velocity over the cross-section.

FIG. 7.



There appears to be no slipping at the walls of the tube. The nature of the change occurring at the critical velocity is exhibited in fig. 7, in which abscissæ are mean and ordinates corresponding actual velocities at the different radii marked on the curves. From these it appears that, below the critical, the velocity at any fixed point is proportional to the total flux, and may be expressed approximately by the formula

$$v = (A - Br^n)v_0,$$

r being the distance from the axis of the pipe, v_0 , the mean velocity, A the ratio of maximum to mean, and B and n constants. In this case

$$A = 1.62, \quad B = 0.0815, \quad n = 3.2.$$

According to the mathematical theory of viscosity* the surface graphically representing the distribution of velocity is a paraboloid, and the equation is of the above form, but having the constants

$$A = 2, \quad B = 2/a^2, \quad n = 2.$$

The two cases are, however, not strictly comparable for, whilst the theory takes no account of terminal conditions, in the experiments these are of importance. There would probably be accelerations and retardations over the cross-section, tending to equalise the velocities and the tubes of flow would not then be strictly parallel to the axis. It is, I think, evident that the variation of the curves from the parabola is in part due to these causes, and in part due to the fact that any resistance or obstruction across the pipe also tends to equalise the velocities. Beyond the critical velocity and within the very narrow limits of these experiments the curves in fig. 7 are approximately parallel when not near the sides of the pipe. At these low velocities, too, the distribution is represented roughly by the equation

$$v = 2.20 - 0.36 r^{2.1} + \left(1.04 - \frac{r^8}{1750}\right) v_0.$$

In practical calculations in Hydraulics it is often assumed that the tangential resistance per unit area in a pipe is

$$\frac{1}{2} f \rho v_0^2,$$

where f is a numerical constant depending on the nature of the surface. Accepting this as an expression of observed facts, Professor Lamb deduces an interesting conclusion.† If v denote the mean velocity at any point, we have at the surface

$$u \, dv/dr = \frac{1}{2} f \rho v_0^2.$$

Now let l be the radial distance between two surfaces moving with relative velocity v_0 in the regular "laminar" flow which would give the same tangential stress, and we find

$$v_0 l = 2\mu/f\rho.$$

In the experiments, the last is the only one to which this formula can be applied. Thus taking $\mu/\rho = 0.0103$, $f = 0.005$, and $v_0 = 8.075$, we have $l = 0.51$ cm. The point at which the velocity is equal to the mean is found from fig. 6 to be almost exactly 0.5 cm., an agreement which is remarkably close for an approximate method.

Summary and Conclusion.—The results may be briefly summarised as follows:—

* Lamb's 'Hydrodynamics,' p. 521.

† *Ibid.*, p. 574.

1. The experiments provide a partial confirmation of the theoretically obtained law of velocity distribution, but show that this distribution can only be obtained under very special conditions, of which absolute freedom from obstructions and end effects are important; and hence

2. When the flow is direct and stream-lines exist, the velocity distribution is not necessarily exactly that which may be described as characteristic of "normal" flow.

3. At the critical velocity the irrotational straight line motion ceases and is followed by one in which the paths of the particles of fluid are eddying and turbulent. The law of distribution of mean linear velocity parallel to the axis simultaneously changes from the parabolic (or approximately parabolic) to that typical of eddying motion.

4. The critical velocity in question (being that at which eddying motion ceases to be transformed into direct motion, and not that at which a highly unstable stream-line motion is suddenly disturbed), is not accompanied by a sudden change in the velocity parallel to the axis at any point in the cross-section. On the other hand, as the total flux increases, the experiments show a gradual transition from one state to the other, due to the change which has occurred in the law of velocity distribution.

5. The observations have little bearing on the upper limit of stream-line flow, as observed by colour bands. They indicate, however, that the unstable direct motion would follow an approximately parabolic law of velocity distribution (as represented by the equation obtained for stream-line motion) and that at the higher critical velocity this distribution would suddenly change to that represented by the equation given for eddying motion. In this case then, instead of a gradual change of velocity, there would actually be sudden and large changes in the velocity parallel to the axis at different points in the cross-section of the pipe.

6. The "Pitot Law" ($v = \sqrt{2gh}$), is at least approximately true at exceedingly low velocities.

In conclusion I must mention my indebtedness to Professor R. M. Ferrier for his uniform kindness during the progress of the work, and for allowing portions of the apparatus to be constructed in the workshops of the College.

The Theory of Photographic Processes, Part II: On the Chemical Dynamics of Development, including the Microscopy of the Image.

By S. E. SHEPPARD, B.Sc., and C. E. K. MEES, B.Sc.

(Communicated by Sir William Ramsay, K.C.B., F.R.S. Received March 25,—
Read March 30, 1905.)

[PLATE 4.]

The investigation of development described in a previous communication* was extended by the application of microscopic methods. The fact that both the silver haloid and the resulting silver are distributed through the film in the form of particles of minute but measurable size, allows us in this way to detect finer qualitative differences in, and to draw independent deductions on the processes of exposure and development. The size of the grain is important, both from the practical point of view and from the theoretical: in the one case as bearing on spectroscopical and astronomical photography, in the other on account of the great importance of the degree of surface-extension for heterogeneous systems.†

The method has been used previously by Abney, Abegg, Kaiserling, Ebert, and others,‡ but by far the most systematic and important inquiry is that of K. Schaum and V. Bellach.§

The work subsequently described had been carried out in part before Bellach's monograph came to our notice. The investigation was then extended beyond the limits of exposure and development given by Bellach,|| and arranged to compare both with his results and those of our former paper. As much of the detail is of chiefly photo-technical interest, only the chief results are given here; a fuller account will be published in the 'Photographic Journal.'

Experimental.

Beck objective $\frac{1}{4}$ -inch and Reichart No. 8 $\frac{1}{16}$ -inch, both dry systems, and for some work Zeiss $\frac{1}{2}$ -inch cedar-oil immersion, kindly lent by Professor

* 'Roy. Soc. Proc.' vol. 74, pp. 447 to 473.

† Ostwald, 'Lehrbuch,' vol. 3 ('Chem. Kinetik'); Bredig, 'Arch. f. wiss. Phot.,' 1900; 'Eder's Jahrbuch,' 1899, p. 357.

‡ H. Ebert, 'Eder's Jahrbuch,' 1894, p. 14; Kaiserling, 'Phot. Mit.,' 1898 (I and II); Abney, 'Phot. Journal,' 1898; R. Abegg, 'Arch. f. wiss. Phot.,' 1899, vol. 1, p. 109.

§ K. Schaum and V. Bellach, 'Physik. Zeitschrift,' 1901—02, and especially "Die Struktur der Phot. Negative," by V. Bellach (W. Knapp, Halle, 1903). This admirable monograph contains a very complete bibliography on all points.

|| Except in region of solarisation.

A. W. Porter, B.Sc. The micrometers were a stage-micrometer in $\frac{1}{100}$ mm., an ocular calibrated on this, and an ocular in squares similarly calibrated.

Emulsion Tests.—As the study of ripening was deferred for further work, only the points bearing on the theory of development were considered. Preparations were made by dissolving a small piece of film in warm water and flattening under a cover-glass, then sealing with Canada balsam. The grains of a very thin layer thus obtained could be examined separately. Long exposure had no apparent effect.

The grain in fast plates varied somewhat in size, there being, *e.g.*, in an Imperial special rapid, two species (α) 0.0011 mm. and (β) 0.0034 mm. The latter were flattened polyhedra, of triangular section; in the slow plates, the emulsion was practically homogeneous, the size of grain in Wratten ordinary being in mean 0.0017 mm. It could not be ascertained with certainty whether the grain was crystalline or amorphous.

The Physical Nature of Silver Haloid Emulsions.—Bellach found that in many cases the mean size of the grain diminished with careful drying.* Thus, after several days' desiccation, a contraction from 0.67×10^{-5} mm.³ to 0.57×10^{-5} mm.³ was noticed in an Eder emulsion. This points to the grain itself possessing structure, and agrees with Quincke's views as to the nature of silver haloid emulsions.† He considers that the AgBr "grains" are not pure AgBr, but contain gelatine. An emulsion in which the colloidal particles have flocked together forms a "spume." Liquid or jellified colloids consist of "spume" masses with liquid or solid spume-walls, enclosing very minute or invisible chambers. In haloid emulsions there is a stiff jelly containing a totally or partially solidified solution of AgBr in gelatine, in which a phase rich in AgBr has separated from a second phase poorer in AgBr, but richer in gelatine.‡ In the spume-walls and cells, spheres and crystals of haloid, much smaller than the measured grain, have separated.

The "adsorption" of gelatine to the AgBr agrees with Eder's researches on the separation of pure AgBr from emulsions by centrifugalising.§

Structure of Developed Negative.

By focussing on the top layer of particles, then down on to the lowest observable particles, the thickness of the reduced silver layer can be measured. This apparent thickness, recorded by the micrometer head of the fine adjust-

* Bellach, *loc. cit.*, p. 34.

† G. Quincke, 'Ann. d. Phys.,' 4te Flge., vol. 2, p. 1000, *et seq.*

‡ Hardy, 'Zeit. f. Phys. Chem.,' vol. 30.

§ Eder and Valenta, 'Beiträge zur Photochemie,' etc., sec. 3, p. 19.

ment, and multiplied by n_1/n_2 , these being respectively the refractive indices of the gelatine and objective systems, gives the real thickness.*

With Wratten ordinary emulsion, exposed and developed as described, the negative-layer was somewhat as described by Bellach :—

(a) Surface-area, particles not very numerous.

(b) Mean-layer, with characteristic forms.

(c) Lower zone of smaller particles, diminishing the lower they lie. This Bellach attributes to the penetration of developer, but we shall show later that a more potent factor is that *the most exposed grains start development first*. On ultimate development these grains reach the same size as the others.

Table I.—N/10 Ferrous Oxalate.

2·0 mins. at 20° C.			10 mins. at 20° C.		
No.	Exposure.	Thickness.	No.	Exposure.	Thickness.
	C.M.S.	mm.		C.M.S.	mm.
2	2·04	0·0226	1	0·101	0·0115
3	4·66	0·0223	2	0·204	0·0116
4	7·75	0·0221	3	0·466	0·0118
5	12·9	0·0223	4	0·775	0·0139
6	27·9	0·0230	5	1·290	0·0195
7	54·5	0·0255	6	2·790	0·0232
8	113·0	0·0241			

Table II.—N/10 Ferrous Oxalate. Time of Development and Thickness.
Exp. = 1·38 C.M.S.

Time.	Density, D.	Thickness.
mins.		mm.
2·0	0·130	0·0200
6·0	0·280	0·0207
8·0	0·349	0·0206
10·0	0·542	0·0203
∞	0·586	0·0203

For the thickness, the following facts were ascertained :—

(a) With constant development for a short time the depth of the image is independent of the exposure.

* Bellach, *loc. cit.*, p. 56.

(b) With increased time of development the depth increases rapidly to a maximum for each exposure, after which it is constant.

(c) With long development the depth increases somewhat with the exposure, a limit naturally being fixed by the thickness of the film.

Every measurement is the mean of 10, each focussing being repeated, and for various portions of the film.

On the Size of the Grain.

Many discordant observations as to the influence of exposure and development on the size of the grain have been published.* Our observations agree with Schaum and Bellach's, for the early stages of development, but on prolonging the development, the conclusions are modified. They may be expressed as follows:—

When γ , the degree of development, is low, the size of grain increases with the exposure.

As the time of development increases, the size of the grain does also, until at γ_{∞} , it is independent of the exposure.

In addition to micrometric measurement of the diameter, the mean size was obtained by drawing the outline of the grains on squared paper by means of a reflecting system,† and then measuring the surface-extension. This method could not be applied to the smallest grains, for which the micrometric measurements are only approximate. The mean diameter of the "area" method is the mean between greatest and least, and is given to compare with the micrometric diameter. The results are the means of 20 observations, and of 10 for the area method.

Influence of Exposure.

Table III.—Developed 2·0 mins. in N/10. Ferrous Oxalate at 20° C.

No.	Exposure.	Micro-diameter.	Area.	Mean diameter.
	C.M.S.	mm.	mm. ²	mm.
1	1·03	0·00114	$1·23 \times 10^{-6}$	0·00101
2	1·87	0·00112	1·45	0·00121
3	3·10	0·00124	1·35	0·00123
4	5·17	0·00135	1·82	0·00130
5	11·8	0·00140	1·90	0·00152
6	22·0	0·00162	2·10	0·00182

Mg = C. 920.

Mg = C. 1360.

* Bellach, *loc. cit.*, p. 72.

† *Ibid.*, p. 76.

For the exposure an intensity-scale was used with constant time. Similar results were obtained by varying the time with intensity constant.

Influence of Development.

Table IV.—Exposure 1·38 C.M.S. Developed in N/10. Ferrous Oxalate at 20° C.

Time.	Density.	Micro-diameter (a).	Diameter (b).
mins.		mm.	mm.
2·0	0·150	0·00103	0·0008
6·0	0·280	0·00124	0·0010
8·0	0·349	0·00157	0·0014
16·0	0·542	0·00160	0·0016
∞	0·586	0·00167	0·0017

(a) For mean layer.

(b) For lower zone.

Size of Grain on Infinite Development.

For moderately high exposures and prolonged development measurements could not be made on the plate direct, so preparations were made and the grain measured and photographed.

Table V.—Developed to γ_{∞} in N/12·5 Ferrous Oxalate.

Exposure.	Density.	Micro-diameter.	Area.	Diameter.
C.M.S.		mm.	mm. ²	mm.
2·04	0·277	0·00145	$1·94 \times 10^{-6}$	0·00135
4·66	0·966	0·00150	2·17	0·00165
7·75	1·496	0·00137	1·90	0·00152
12·90	2·400	0·00156	2·14	0·00171
27·90	3·400	0·00149	1·90	0·00159
54·30	4·39	0·00151	2·18	0·00165
209·0	—	0·00140	2·03	0·00156

Hence, generally, $G = \phi(\gamma, E)$, but at γ_{∞} G is independent of E , the exposure. (See Plate 4, figs. I and II.)

Effect of Bromide.

Table VI.

No.	Exposure.	Diameter A.	Diameter B.
	C.M.S.	mm.	mm.
1	1·01	0·0009	Absent
2	2·04	0·00094	Points
3	4·66	0·00105	Points
4	7·75	0·00114	0·0008
5	12·90	—	0·00085
6	27·9	0·0143*	0·00103
7	54·5	—	0·00123
8	113·0	0·0165*	0·00145

* From preparations.

These were developed 1·0 minutes in N/10 ferrous oxalate, A, no bromide, B, N/200 K.Br.

This confirms Bellach's statement that bromide lowers the size of the grain. In addition, it should be noticed that the effect is greater the less the exposure. Also, it was found that the size of the grain diminished as the concentration of the bromide increased.

*Bromide at Infinite Development.*Table VII.—Developed to γ_{∞} in N/10 Ferrous Oxalate, N/200 KBr.

No.	Exposure.	Micro-diameter.	Area.	Mean diameter.
	C.M.S.	mm.	mm. ²	mm.
1	2·04	0·00142	$1·7 \times 10^{-6}$	0·00135
5	27·9	0·00137	1·9	0·00142
8	209·0	0·00172	2·0	0·00139

Mg = 920.

Mg = 1300.

On comparing this table with Table V, it will be seen that on infinite development the grain attains the same size in a bromided as in a non-bromided developer. (See Plate 4, figs. III and IV.)

On the Number of Grains and Exposure.

In the Surface Area.—For this, photo-micrographs were taken at 500 diameters, and the grains counted in a given area on the negative. The values are the means of 20 observations.

Table VIII.—Developed 10 mins. in N/10 Ferrous Oxalate.

No.	Exposure.	No. per visual area.	No. per 1 mm. ² film.
	C.M.S.		
2	0·187	17·1	192×10^3
3	0·310	16·2	181
4	0·517	18·8	211
5	1·18	17·8	199

Hence for moderately long development, the number of grains on the surface is constant.

In the Thickness.—These were counted directly under the microscope, with a micrometer in squares. The values are for 25 to 30 squares, readings being taken in different portions of the film. The unit volume is a prism of area 1 mm.² and height equal to thickness of film. It was found that the *number of grains increased with the exposure, and for moderately long development was nearly proportional to the density.* As this is contrary to Bellach's results, several sets of experiments were made, with as wide a range as practicable of exposure and development, which fully bore this out. The conclusion was further tested by making sections through the film. The best results were obtained by removing the developed film from the plate and rolling it up in gum mucilage. A small portion was then frozen on an ether spray microtome and sections cut. These gave a spiral embracing several tones, and it was easily seen that the number of grains increased with the exposure, the depth of the image but slightly. The appearance agreed with Abney's description:* "With small exposure the grains are congregated chiefly near the surface. As the exposure increases, the film behind fills up with particles and they crowd together."

Table IX.—Developed 6·0 mins. in N/10 Ferrous Oxalate.

No.	Exposure.	No. per 100 mm. ² visual.	Per unit vol.
	C.M.S.		
1	0·04	2·90	$27·3 \times 10^3$
2	0·081	2·46	23·4
3	0·184	3·21	30·2
4	0·312	6·10	57·5
5	0·52	7·58	71·0
6	1·12	8·34	78·5

Mg = C. 1000.

* Abney, 'Phot. Journal,' 1898.

1 and 2 were below the "Schwellenwerth." Obviously the number increases with the exposure. This was confirmed for other experiments, as far as the density permitted. Above 0.3 to 0.4 measurements could not be made; but it can be seen that on extreme development (Table V) the size of the grain is constant. Yet the density has increased from 0.277 to 4.39 or about sixteen times. Since no commensurate increase in the size of the grain has occurred, the number must have increased.

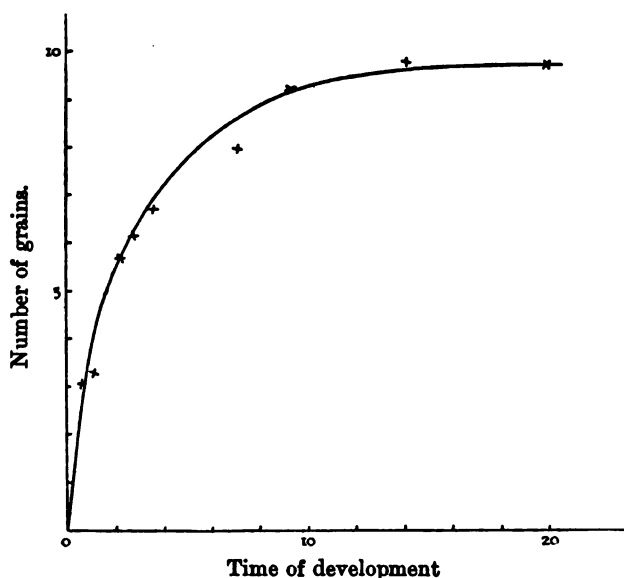
Influence of Development.

Table X.—Wratten Ordinary Plate Exposed for 0.25 C.M.S. developed in N/10 Ferrous Oxalate at 20° C.

No.	Time.	No. of grains per 100 mm. ² visual.	Per unit vol.
	mins.		
1	0.5	3.35	31.5×10^3
2	1.0	3.54	33.3
3	2.0	6.10	57.5
4	2.5	6.45	62.5
5	3.5	7.20	67.8
6	7.0	8.58	80.8
7	9.0	10.03	94.5
8	14.0	10.50	99.0
9	20.0	10.40	98.9

See Curve I.

Curve I.



The number of grains increases rapidly at first, then more gradually till a maximum is attained. This agrees with Bellach's results.

Exposure Through the Glass-side.

Two plates were given identical exposures behind the sector-wheel, and developed for 10 minutes in N/10 ferrous oxalate at 15°. One was exposed through the glass-side, the other from film-side but with a glass plate in front. On fixing, etc., although both showed 5 tones, the densities of the glass-side plate were considerably less than that of the other. This agrees with Abegg* and Bellach.†

Thickness of Negative-Layer.

No.	Exposure.	Thickness (a).	Da.	Thickness (b).	Db.
	C.M.S.	mm.		mm.	
1	10	0·0204	—	0·0192	—
2	5	0·0199	0·110	0·0180	0·257
3	2·5	0·0188	0·042	0·0153	0·098
4	1·25	0·0181	—	0·0152	0·027
5	0·62	0·0148	—	0·0152	—

(a) Glass-side.

(b) Air-side.

The depth is much the same for both plates. According to Abegg, all the grains in back exposed plate appeared equally developed, whereas Bellach describes his preparations as similar to front exposed plates, i.e., uppermost zone with few and small particles, mean characteristic layer, and lowest with very small particles. In our plates the appearance agreed with Abegg's description, the increase in size of grain being in the opposite sense to that of a film-side exposed plate. The apparent divergence in description is probably due to the fact that Bellach used short development, 110 seconds, with a strong developer, while Abegg used prolonged stand development, more comparable with the author's conditions. The result shows, that other things being equal, *the grain receiving most exposure is most reactive and starts development first.*

Thus, for 1·25 C.M.S. exposure,

	Micro-diameter. mm.	Focus. div.
Film-side plate	{ 0·00135 0·0008	76·0 74·6
Glass-side plate	{ 0·00106 0·00140	79·5 77·0

* R. Abegg u. Cl. Immerwahr, 'Sitz. ber. d. Wien. Akad.,' vol. 114, abt. 2A, 1900.

† *Loc. cit.*, p. 61.

The number of grains was greater in the plate exposed from air-side. For 1 mm.² of film,

Air-side.....	132 × 10 ³ ,
Glass-side	71 × 10 ³ ,

while Abegg and Immerwahr give 41.0×10^3 and 32.5×10^3 . Both the densities and the number of grains are greater for the air-side plate. Abegg attributes this to the prevention of halogen diffusion. Braun's* observation on the part played by oxygen in the formation of latent images may also account for it however. Possibly connected with this is the statement of Wulf,† that for the so-called photo-electric effect the sensitiveness to light increases as the potential fall of electrode to surrounding gas increases.

The general results of the microscopic survey are in agreement with the theory of development proposed before. Each grain develops as a more or less isolated system, only uniting to form "aggregates" with other grains at high exposures, when the packing is closer. The thickness of the reaction-layer is from 0.02 to 0.04 mm., a value similar to that found by Brunner for many heterogeneous reactions. But in this case *the solid phase lies entirely in the layer*. The diffusion of the developer may be divided into two parts:—(a) through the total thickness, δ , (b) through the micro-layer, δ' , of the order 0.0005 mm. surrounding the grain. This is the true reaction-layer, and the reaction is somewhat like to the catalysis of H_2O_2 by colloidal metals, save that there is no convection. As the diffusion has to take place through gelatine, the structure and state of this may influence the velocity. This will be dealt with later. The fact that the size of the grain with low time of development—or better—low development-factor varies with the exposure, indicates that the "reactivity" of the individual haloid grain is a steady function of the exposure. Hence at low development-factors departures from the law of constant density-ratios are possible, but difficult to confirm. *Such departures will be the more marked whenever the chemical-velocity approaches that of the diffusion process.*

The conclusions given here were confirmed for other developers, and we hope to publish them later in connection with the general survey of these; since this work was finished, Messrs. Lumière‡ and Wallace§ have published short studies on the size of the grain. Their results do not contradict ours, but they do not seem to have considered sufficiently the effect of the degree of development, γ , on all observations.

* Braun, 'Zeitschrift f. wiss. Phot.,' vol. 2, Heft 8.

† Th. Wulf, 'Ann. d. Phys.,' 4te Flge., vol. 9, p. 946.

‡ Lumière, 'Zeit. f. wiss. Phot.,' vol. 2, p. 256.

§ Wallace, 'Astrophysical Journ.,' 1905.

The early stages of development.—Considerable information concerning the velocity of development can be obtained from the “time of appearance” of the image, which is a function of it. In 1893 Mr. Watkins announced that for any given reducer the time of appearance gave an accurate indication of the speed of working, and that any variation in the alkali, temperature, or strength affected the time necessary to reach a given density or development-factor in the same proportion that it affected the time of appearance. Generally stated, $T_D = WT_A$, where T_D is time for density, D . T_A is time of appearance, and W is a constant.

This rule has been usefully applied in practice for timing development, but the above statement is too wide, both experiment and theory showing that such a simple relation does not hold for many complex developing solutions. The following considerations from the theory of the order of reactions* explain both the rule and the deviations from it.

If two analogous reactions continue to equal fractions of the total change, then the times necessary for this are inversely as the velocity-factors.

Of course, it is assumed that the same function of the variables still represents the course of the reaction. If experiments with different concentrations are carried to the same fraction of these, the following relations hold:—For reactions of the first order the factors are directly, the times inversely as the concentrations, of the second order as the squares, and so on. We may apply this to development as follows:—The density which is first visible, *i.e.*, first distinction between exposed and unexposed, is a physiological constant and a fixed density, θ , say (Schwellenwerth).† Hence for same exposure, *i.e.*, same final density, θ is always an equal fraction of the total density; so \mathfrak{S} , the time of appearance, *i.e.*, for density, θ , is inversely as the velocity-coefficient, and is similarly modified by concentration, etc.

With different final densities and constant developer, the values of \mathfrak{S} are inversely as the final densities, D_1 , D_2 , etc. Here, of course, θ measures an equal fraction of the total oxidation of reducer.

Let D_1 and D_2 be any two final densities, and λ a fixed density, where D_1 , D_2 = or $> \lambda$, and let \mathfrak{S}_1 and \mathfrak{S}_2 be their respective times of appearance, and t_1 , t_2 corresponding times to reach λ . Then we have

$$t_1/\mathfrak{S}_1 = t_2/\mathfrak{S}_2 = t_\lambda/\mathfrak{S}_\lambda = \text{constant } W,$$

whose numerical measure is proportional to the Watkins multiple, and is independent of concentration and only dependent on velocity function.

* Ostwald, ‘Lehrbuch,’ 2te Auflage, vol. 2, p. 236.

† This fact rests on the existence of a “Schwellenwerth” or “threshold” value of perception of contrast by the eye.

The general theorem is only true for simple reactions, and does not hold for "graded," "catalysed," and so forth. *The same limitations hold for development*, and the occurrence of initial disturbances, varying in the specific developers, probably account for the wide variation of the Watkins multiple for various developers, and also its variation with the same reducer. *Only for developers* in which the balance between reduction-potential and diffusivity is within certain limits will W be constant, since deviations will easily occur for such a small fraction of the total change, and yet the development-function remain much the same.

The writers have extensively developed the use of the "time of appearance" for investigation of development-kinetics. The most similar use of such a method of inquiry in chemical dynamics is A. von Oettingen's* research on the decomposition of thio-sulphate by acids, in which the "time of appearance" of the sulphur-cloud was observed. The limiting conditions for experimental accuracy discussed there hold also for development. The time must not be so short that the limiting error of measurement seriously affects the result, nor so long as to cause doubt as to the exact moment. The observations are made in a dark-room, but using as much of a steady reddish light as possible, since subsequent fogging is in general immaterial.

The timing was done with a stop-watch marking $\frac{1}{5}$ of a second; several observations of each time were made, and the mean used, and all measurements for comparison made at one period. The method is accurate within the limits employed to about 2 per cent.

Effect of Concentration with Ferrous Oxalate.

Table XI.—Plate, Wratten Ordinary, exposed 8 C.M.M.

Concentration.	T_A in secs.	Mean T_A .	$C = \text{Product.}$
0.2 N.	22.0, 19.0, 19.0, 18.8	19.7	3.94
0.1 N.	40.4, 40.0, 40.2	40.1	4.01
0.05 N.	81.0, 79.8, 80.5	80.4	4.02
0.025 N.	160.2, 158.2, 157.0	158.4	3.96
			Mean 3.98

This shows from $N/5$ to $N/40$ the velocity is directly proportional to the concentration, even at this early stage of development.

* 'Zeit. f. Phys. Chem.,' vol. 30; cf. also H. Landolt, 'Ber.,' vol. 19, p. 1317, 1886.

Temperature and Development-Velocity.

Experiment showed that the variation of temperature did not influence the density-ratios. The effect of temperature on the velocity-constant $K = \frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ was measured, and also on $V = 1/T_A$. In this case four series of measurements were made, embracing the range 0° C. to 30° C. By interpolation the reduced results gave the following table.

Table XII.—Developed in N/12.5 Ferrous Oxalate.

Temperature, ° C.	Absolute.	Velocity.	V mean.
-0.8	272.2	1.00	1.00
0.0	273.0	1.01	1.01
5.2	278.2	1.29	1.29
6.7	279.7	1.33	1.33
9.2	281.2	1.42, 1.56, 1.51	1.50
15.0	288.0	2.126	2.13
20.0	293.0	2.50	2.50
25.0	298.0	3.29	3.29
30.0	303.0	4.35	4.35

Van't Hoff's equation $\frac{d \log K}{dT} = \frac{A}{T^2}$ in the integrated form for A sensibly constant, $\log K = -\frac{A}{T} + C$ was found to represent the results very fairly.

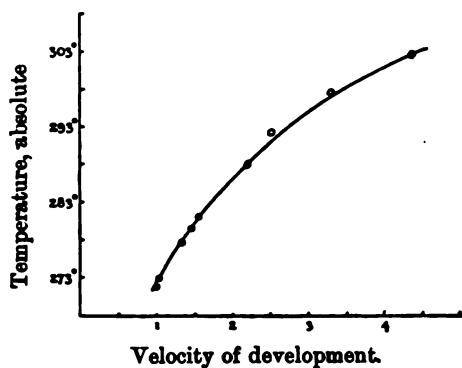
Table XIII.—C found as 7.60.

Temperature.	A.	V obs.	V calc.	Δ per cent.
272.0	1794	1.00	0.982	-1.8
273.0	1798	1.01	0.991	-1.9
278.2	1807	1.29	1.290	0.0
279.7	1911	1.33	1.380	+4.0
281.2	1806	1.50	1.506	+0.4
288.0	1806	2.13	2.133	+0.1
293.0	1817	2.50	2.69	+8.0
298.0	1813	3.29	3.467	+5.0
303.0	1807	4.35	4.361	+0.25

Curve calculated from $\log K = -1806/T + 7.60$.

* J. H. van't Hoff, 'Kgl. Svenska Vet. Hdl.,' vol. 21, No. 17, 1885.

Curve II.



The temperature-coefficient for 10° from 0° to 30° C. is $(K+10^\circ)/K = 1.7$.

The validity of these results is shown by measurements of K , the mean velocity coefficient.

Table XIV.

Temperature, °C.	K found.	K calc.	Δ per cent.
9.6	0.0632	0.0632	—
20.8	0.0870	0.0891	+2.2
30.7	0.1174	0.1210	+2.0

The Temperature-Coefficient.

Bodenstein* and Senter† have indicated the value of the temperature-coefficient for 10° as a criterion in heterogeneous reactions. For chemical reactions in homogeneous solution the value is generally about 2 to 3,‡ while Brunner found 1.5 for rate of solution of benzoic acid in water; for diffusion-processes we should expect a value about 1.5, and not varying for different bodies very much.

Now we have found that the expression $K = \frac{1}{t} \log \frac{\gamma_\infty}{\gamma_\infty - \gamma}$ can be used to measure the development velocity for most developers. A preliminary study of the temperature-coefficient for different emulsions and developers gave the following results:—

* 'Zeit. f. Physik. Chem.,' vol. 49, p. 42, 1904.

† 'Roy. Soc. Proc.,' vol. 74, p. 214.

‡ Van't Hoff, 'Vorlesungen,' vol. 1, p. 225.

Table XV.

Reducer.	Emulsion A.	B.	C.
Fe(C ₂ O ₄)	1·60	1·90	1·70
FeF	1·52	—	—
Fe Citrate	1·54	—	—
C ₆ H ₄ (OH) ₂ p	—	2·10	—
C ₆ H ₄ (OH) ₂ o	—	2·80	—

The temperature-coefficient frequently passes the value to be expected from the diffusion-theory. But in the case of development, we must be cautious in applying the criterion, as the following consideration will show :—

Beside the increase in diffusivity (mobility of reducing molecule), we must also consider (a) alteration of resistance to diffusion in gelatine; (b) in complex developing-solutions, alteration of concentration of reducing ion by changing the chemical equilibrium, especially in alkaline developers. Under these conditions a *high temperature-coefficient in development does not necessarily mean that the velocity is that of a chemical reaction.*

In the case of ferrous oxalate, the theoretical formula of Van't Hoff, which is a deduction from the reaction-isochore, was employed. This is not legitimate in the case of diffusion phenomena, and the best formulation would probably be the ordinary parabolic interpolation formula in the form $K_t = K_0(1 + at + bt^2)$; a comparison of the constants a and b for different plates and developers should yield useful information on temperature influences.

Resistance of the Gelatine.

Hardening agents, which raise the melting point of the gelatine, are generally supposed to alter the velocity of development by changing the diffusivity. Many emulsions, however, show no such effect. Thus, with formalin (40-per-cent. formaldehyde) in 4-per-cent. strength and increasing time of immersion, although the film became quite insoluble in boiling water, the development-velocity was not lowered.

The general theory of the action of hardening agents will be discussed later in connection with the destruction of the "latent image."

Table XVI.

No.	Time of immersion.	T_a in secs.	Mean.
	secs.		secs.
1	0	24·0, 23·2, 24·0	23·7
2	30	24·0, 24·2, 23·8	24·0
3	60	24·0, 24·2, 23·4	23·9
4	120	23·6, 24·6, 24·0	24·0
5	240	24·0, 23·0, 23·4	23·4
6	8 per cent 10 mins.	25·2, 23·4	24·3
			$T = 23·9$

"Penetration" of Developer.

By the rate of penetration the time for the reducer to pass through the reaction-layer, δ , is understood. This was studied as follows:—

If plates are exposed through the glass-side, the image will lie nearer the glass, and we may expect it to appear—

- (a) On front first if the penetration of the developer count most.
- (b) On back first if the greater reactivity of the more exposed particles be the predominant factor.

A strip of Ilford ordinary film was exposed, cut up, and developed in N/10 ferrous oxalate at 15° C.

The values of T_a given are means of four experiments.

Table XVII.

Exposure.	T_a film-side.	T_a glass-side.
Ilford film—		
300 C.M.S.	40·3 secs.	45·3 secs.
60 „	54·6 „	52·6 „
10 „	72·4 „	63·0 „
Wratten ordinary—		
300 C.M.S.	94·2 „	90·4 „

Consequently, with low exposures, the back appears before the front, but as the exposure increases, the developer being the same, the two times become equal, and eventually the image appears on front first. This was confirmed on plates exposed in the sensitometer.

Plates given the same exposure from the front always show the image from the front first, the relative difference in time being somewhat greater, the absolute value of T_a always less.

The above phenomena may be explained by the following considerations drawn from the microscopy of the image :—

(a) The absolute thickness of the layer of developable particles increases but slightly with the exposure.

(b) Reckoning down through the layer from the exposed side, the reactivity of each layer of grains diminishes through the thickness. *The slope of this reactivity-gradient then depends upon the exposure.*

(c) With short time of development the penetration increases rapidly ; further, as the developer reaches the lowest layers, its concentration will be diminished somewhat by diffusion and oxidation by developable AgBr. There will, therefore, be a concentration gradient through the film.

(d) Then in the case of exposure from air-side, the two gradients will be in the same direction, and will reinforce each other ; for exposure from the back, the gradients will be opposite in sense, and the front layers or back will appear first according as one factor or the other predominates.

This result is in agreement with the microscopic deduction, that other things being equal, the more exposed grains possess the greater reactivity and start developing first.

With regard to the absolute time required for the developer to penetrate the thickness of the film, an estimate can be obtained as follows :—With an Ilford film, the γ, t curve of which was known, the *least* time of appearance at the back for any exposure through the back was about 10 seconds with N/10 ferrous oxalate at 15° C. Now, under these conditions, the half-period of development, i.e., for $\gamma_\infty/2$, was 5.0 minutes. Hence, the error due to incomplete penetration is not of a very large order, and, moreover, reasons will be given later for assuming a chemical-induction generally greater than any diffusion-induction. However, for accurate comparison of velocities, in order to avoid an erroneous time-zero, the form

$$K = \frac{1}{t_2 - t_1} \log \frac{\gamma_\infty - \gamma_1}{\gamma_\infty - \gamma_2} *$$

is the most suitable.

In development the temperature-coefficient has been found an inadequate criterion for distinguishing diffusion from chemical-velocity. Such a criterion, however, we believe to exist in the action of soluble bromides, and in a discussion of this and the reversibility of development we hope to

* Senter, *loc. cit.*, p. 203 ; see also Ostwald-Luther, 'Physico-chem. Messungen,' p. 455.

show that the development process probably takes place in general in two phases, in the first period the chemical-velocity being slow compared with diffusion, in the second the contrary holding. It is the velocity of the second period which is usually measured.

In conclusion we have much pleasure in expressing our great thanks to Sir William Ramsay, F.R.S., for his interest in the investigation.

DESCRIPTION OF PLATE.

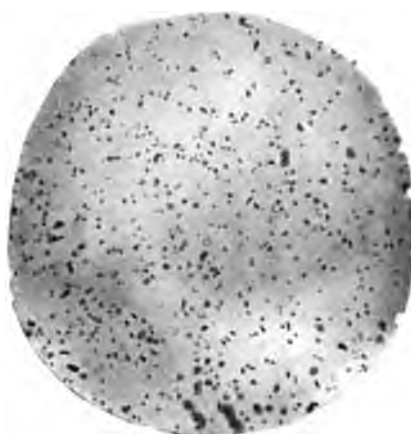
Figs. I to IV are from preparations as described on p. 217, etc.

Fig. V was photographed directly from the Plate and shows the grains *in situ*; the large "aggregates" are as much due to superposition of grains as to physical fusion.

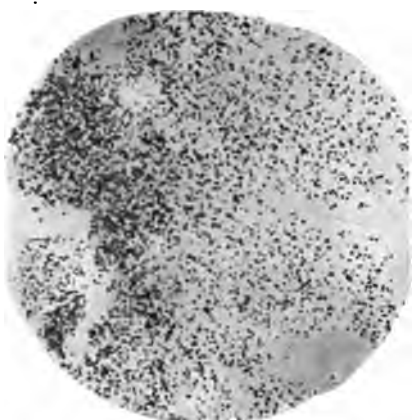




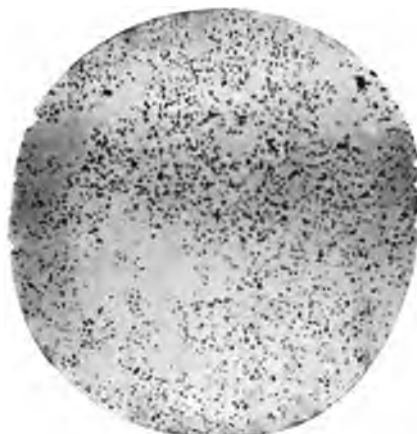
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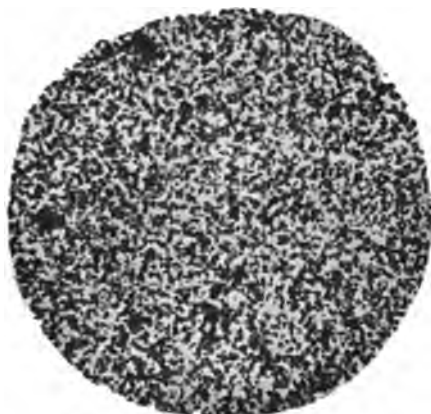
II



III



IV



V

I, II for γ_{∞} , 209 C.M.S. and 2 C.M.S.
 III, IV, ditto ditto ditto
 in N/200 KBr.
 Mg., C. 900.
 (See Tables V and VII.)

V, 1.38 C.M.S., dev. 10 minutes.
 in N/10 FeOx at 20° C. Mg., C. 900.

*On a New Type of Electric Furnace, with a Redetermination of
the Melting-Point of Platinum.*

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National Physical Laboratory, Teddington.

(Communicated by R. T. Glazebrook, D.Sc., F.R.S., from the National Physical
Laboratory. Received March 21,—Read April 13, 1905.)

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I.

An investigation is now in progress in the thermometric department of the National Physical Laboratory, having for its object the design of an electrical method of measuring temperatures from 1200° C. upwards in some such way as temperatures below this value may now be determined by an appropriate thermocouple or resistance thermometer. It is, of course, common knowledge that metals such as platinum and alloys of the platinum group are unable for prolonged periods to withstand, without alteration of their structure and properties, the effects of temperatures above about 1200° C., particularly if in presence of even small quantities of certain gases, such as are very difficult to ensure shall be completely absent, especially at the higher ranges. This is the case with nearly all methods of heating, whether electrical or otherwise.

The brilliant researches of Moissan on the stability of all kinds of substances at very high temperatures, and the recent work of Nernst culminating in the invention of his well-known lamp, in which the light-

giving filament is formed of a complex mixture of oxides of rare earths, directed the attention of the author to this class of bodies. From a study of their behaviour he has been able to work out a method of attaining by very simple means very high temperatures, which may be controlled with great ease. A preliminary account of this new type of electric furnace, with some results of investigations undertaken with it, forms the subject-matter of the present paper.

II.

The author was unaware at the outset of the work that the fairly obvious idea of making large tubes of solid electrolytic conductors had been previously applied, and had come across no accounts of any previous work in the usual scientific journals, but during the progress of this investigation he has found, by searching in the patent literature of England, Germany, and the United States, that more than one investigator has been working on the subject.

Nernst himself mentions the idea of using a tube, and H. N. Potter, in 1902, took out American patents for a tube furnace on this principle, designed for the baking of Nernst glowers in lamp manufacture. He appears to have had difficulties in getting uniformity of specific resistance throughout the tube, and suggests building up the wall in insulated sections, each fed from an appropriate circuit with series resistance.

Mr. Solomon, of the British Nernst Light, Limited, also used small tube furnaces of the same kind for the baking of glowers. His furnace tubes, about 9 mm. interior diameter and 100 mm. long, after being formed and treated to render them initially conducting, were mounted in a small copper trough in pure powdered zirconia, and heated by a gas burner. Such a tube when cold has, after drying, a resistance of at least 1000 megohms, but from about 400° C. upwards this falls off so rapidly that on a 250-volt circuit it will light up at a low red heat, the gas being then extinguished. At the highest safe-working temperature such a tube drops about 100 volts with a current of 5 to 6 ampères. After having had the benefit of Mr. Solomon's experience, with numerous excellent hints from him as to experimental details, the author built and studied the behaviour of a number of these furnaces. Experience showed that the point in them most likely to fail was the contact between the platinum electrode and the tube. Further, that the material had a very large coefficient of expansion, and that, probably largely on this account, severe strains were set up between the outer and inner layers on fairly rapid heating and cooling, thus tending to make the life of such a furnace very uncertain.

In order, therefore, to avoid the necessity of having contacts on the tubes capable of carrying relatively large currents, and the consequent severe strain on the parts, the author conceived the idea of reaching the high temperature desired by a "cascade" arrangement such as is familiar in all the older methods of obtaining low temperatures. To reach a temperature of 2000°C ., it was, therefore, arranged to only put through the tube itself sufficient energy to raise its temperature 1000°C . above its surrounding, and to keep the surrounding itself at about 1000°C . by means of a protecting jacket heated in any convenient way by an independent electric circuit.

III.

Fig. (1) shows the arrangement adopted in the small type of vertical furnace used in the experiments detailed later. AB is the central conducting tube, which in this case was about 10 mm. internal diameter and 60 to 70 mm. long. CD is a tube of hard porcelain or other suitable refractory

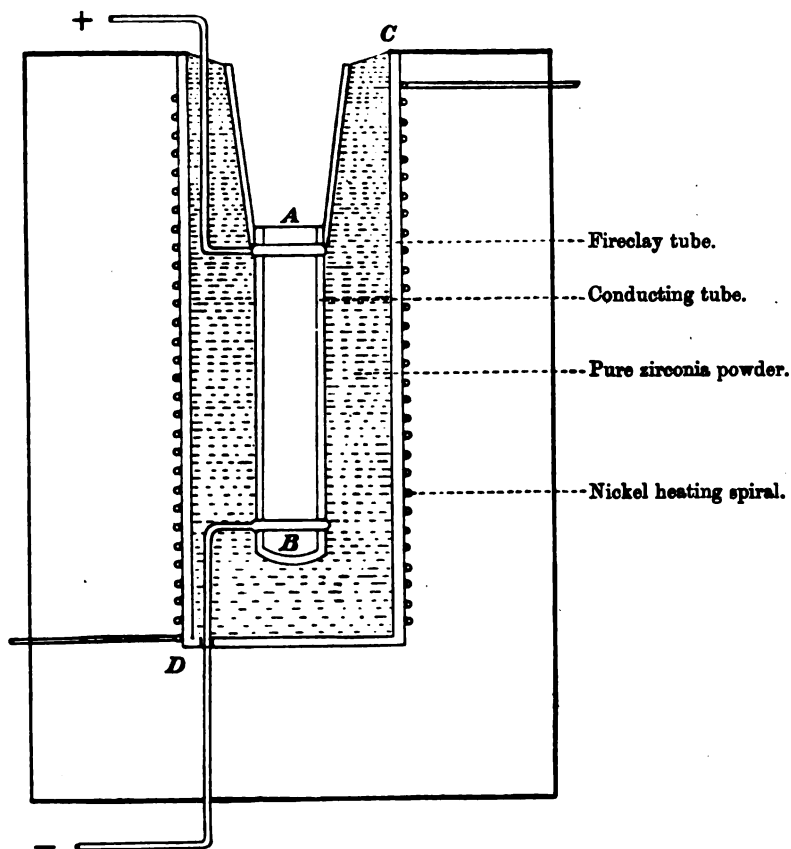


FIG. 1.—Diagrammatic sketch of furnace for platinum melting-point determinations.

material, 30 to 40 mm. internal diameter, on which is wound the heating spiral of nickel wire, protected from oxidation by some suitable means. The space between is filled with powdered zirconia, which should not contain any appreciable admixture of any other substance, otherwise it gradually becomes a conductor at very high temperatures. When the furnace is in action, in this layer of zirconia there is a falling gradient of temperature from the centre outwards, which suffices to prevent the nickel spiral from becoming unduly heated by radiation from the inner tube. The current is led into the tube by platinum flexibles, enveloping it at A and B and joined by autogen soldering to nickel or platinum wires leading to suitable terminals.

To a similar pair of terminals on the nickel wire heating circuit is connected an appropriate source of current with regulator and ammeter.

To enable the tube to be heated fairly uniformly to above the upper electrode, it is sunk 20 or 30 mm. below the level of the top of the nickel spiral, and a mouth-piece of rather wider unglazed porcelain tubing is slipped over its upper end, which can be closed if necessary by a stopper. A capillary tube, made of the same mixture as the furnace tube proper, may be fitted below for the introduction of any gas desired.

To light up such a furnace current sufficient to dissipate 100 to 300 watts is passed through the nickel spiral, the safe maximum amount of energy supplied during the heating up of furnace depending on the details of construction and the nature of the protecting medium in which the nickel is buried. As a rule, less than half-an-hour suffices to bring the central tube to a red heat. The terminals of the tube are meanwhile connected to the supply of current at from 200 to 500 volts.* Since the temperature coefficient of practically all solid electrolytic conductors is negative and very large, the current in them becomes unstable at very high temperatures, unless a sufficient steadying resistance is always left in series with them. For furnace work it suffices if 20 to 25 per cent. of the whole volts of the circuit are dropped on the series resistance.

Care should be taken with furnaces run for long periods at very high temperatures that the temperature of the electrodes does not rise beyond the melting-point of platinum. Though this is easily arranged for in the design of small tube furnaces, it becomes more difficult to ensure in those of larger size. In these the conductor is arranged in the form of a reel, the electrode wires wound round the wider part at the ends being thus more easily kept relatively cool.

* Short furnaces can be lit up on a 100-volt circuit.

IV.

In the type of furnace just described, when about 150 joules are generated in the jacket circuit, a current of about 2 ampères suffices to take the central portion to about 2000° C., the volts dropped on the tube depending on the distance between the electrodes and the condition of the tube material, but rarely exceeding 100 volts at the higher temperatures, and often being only 60 or 80. It was found that with a well designed regulating resistance, the control of the temperature of the inner walls of these surfaces was so perfect between 800° and 2000° C., that well-defined melting-points could be obtained in them on very small quantities of substance. Using a suitably supported thermojunction of bare platinum, with platinum-rhodium or platinum-iridium, it was found possible, even with fairly rapid heating, to obtain very concordant values for the melting-point of the platinum wire forming the junction. It was further obvious that, if the melting-point of platinum were accurately known, this method would furnish an excellent and easily determined high temperature fixed point for thermojunction standardisation.

V.

Having in the laboratory a considerable number of specimens of platinum and platinum alloys of different composition from different sources, some of which had been accurately studied as thermojunctions over a large range, a selection was made from these of a number of characteristic specimens, giving widely different electromotive forces, and the formula connecting the thermoelectromotive force with temperature was carefully determined for each. In most cases this was done by direct comparison in a specially arranged electric furnace with the laboratory standards, from somewhat below 400° C. to over 1250° C. In certain other cases the standardisation was made by means of selected fixed points. The details of these methods of standardisation and of the potentiometer used, which was specially designed for thermoelectric work, were described in the author's earlier paper on the "High Temperature Standards of the National Physical Laboratory," published in the 'Phil. Trans.' for 1904, vol. 203, pp. 348 to 384. As a measure of the accuracy attained it will suffice to say that the coefficients for the type of formula

$$Et = -a + \beta t + \gamma t^2$$

were calculated by least squares for each junction from the observations made, and that in a comparison of six junctions with two standards embracing 10 to 12 temperatures spaced fairly regularly between 400° and nearly 1300° C., it was seldom that the difference between the observed values of the E.M.F. of any junction at any point, and the value of the E.M.F. for that temperature

calculated from the formula, differed by as much as 1° C., and in no single case exceeded 2° C.

The type of formula chosen is the same as is given in the paper previously referred to, and the scale of temperature adopted is the one there defined, which was shown to agree within the limits of error with the scale of temperature used at the Reichsanstalt, as established by the experiments of Holborn and Day. Below 300° C. a formula of this kind having a term which does not vanish when $t = 0$; does not represent the E.M.F. exactly, since from about this temperature downwards there is a marked change in the curve of E.M.F. for all junctions made of the platinum metals, and on this account, therefore, it is not permissible to use any of these formulæ for downward extrapolation except over quite a limited range.*

VI.

The experiments with each junction were made as follows:—The two wires selected were melted together in a small oxidising oxyhydrogen flame, and after cooling the whole was mounted on a convenient insulating stand with fine adjustments. The "hot" junction was brought to a central position in the heated furnace at an appropriate height, and the two "cold" junctions were placed in glass tubes in ice.

The observer then followed the rise of E.M.F. on the potentiometer while an assistant gradually increased the furnace current as required. When the melting-point of platinum was reached, if the rate of rise were not very much too rapid, an exceedingly well marked halt was obtained. During the halt, the duration of which depended of course on the rate of heating of the furnace, one of three things usually happened, the particular phenomenon observed depending on the relative position, diameter and state of tension of the wires forming the thermocouple.

Either, first: The wires sprang away from one another, one of them usually coming into contact with the side of the tube. The moment when this occurred was always easily recognisable on the potentiometer.

Or secondly: A globule of molten platinum formed on the end of the wires. This sometimes attained such dimensions as to drop off, thereby breaking contact.

Or possibly, third: The globule of platinum formed gradually climbed up

* Professor Callendar in his article on thermoelectricity in the supplementary volumes of the *Encyclopædia Britannica* says "Holborn and Day have gone back to Tait's method at high temperatures, employing arcs of parabolas for limited ranges. But since the parabolic formula is certainly erroneous at low temperatures, it can hardly be trusted for extrapolation above 1000° C." The results given later seem, however, to render it highly probable that, contrary to expectation, *upward* extrapolation is justifiable.

the rhodio-platinum or iridio-platinum wire, to a higher position in the furnace. During its movement, small temperature oscillations are observed on the potentiometer, amounting to perhaps 2° or 3° . The molten platinum did not appear to sensibly attack the other wire, any irregularities on its surface being practically as sharply marked after the experiment as before it and its total length remaining unaffected.

Provided the furnace wall near the junction were nowhere allowed to rise beyond the melting-point of the *platinum-rhodium* or *platinum-iridium* wire (which with 10 per cent. alloys is in each case much above that of the pure metal), the temperature attained by the drop of molten platinum, whichever of the above alternatives happened, was very steady and independent of the current in the furnace. There was usually no difficulty in repeating the setting of the potentiometer-slider for the same junction, without looking at it, to less than 1° C., if the conditions are not greatly changed. Provided the immersion in the furnace is sufficient, and that there is an ascending gradient of temperature from the furnace mouth downwards, varying the immersion considerably makes no difference in the point of balance attained. After having had the method once explained, an observer not familiar with the apparatus, who was quite unprejudiced as to what value of the thermal force or temperature to expect, was able at once to take an observation, agreeing to within about 2° C. of the mean value previously obtained from a number of experiments with the junction in question.

VII.

In Table I (p. 242) a summary is given of the values obtained in 66 determinations made on the melting-point of platinum, no observations recorded in the note-book having been arbitrarily rejected.

Three different furnaces were used—a few experiments having been made in one arranged horizontally—and for many of the junctions perfectly independent determinations were made on different days. For the sake of better showing the degree of concordance obtained, the individual observations made with junction T₉, a commercial 10-per-cent. iridium of medium thickness—the first set taken—are given in Table II (p. 242). This set were all made on one day, but by three different observers, one of whom had had no previous experience of the method.

Table I.—Summary of Determinations of the Melting-Point of Platinum

Junction.	Date.	Observers.	No. of experiments.	Highest value found.	Lowest value found.	Mean.
T ₉	1904— September 16 ...	J. A. H. W. H. H. C. H. C.	7	1713	1709	1711
	September 16 ...	J. A. H.	4	1709	1707	1708
N. P. L. 3	September 20 ...	R. T. G.	9	1714	1709	1712
	October 13	J. A. H.				
T ₁₄	October 25	J. A. H.	14	1707	1703	1705
T ₁₅	1905— January 16					
	January 28					
	1904— October 25	J. A. H.	10	1712	1703	1707
	October 27					
	1905— February 6					
	January 16	H. C. H. C. J. A. H.	8	1705	1702	1704
	January 16	H. C. H. C. J. A. H.	3	1693	1691	1692
	January 28	J. A. H.	13	1698	1694	1696
T ₂₀	January 31					
T ₂₁	January 31	J. A. H.	3	1713	1711	1712

Table II.—Observations on Melting-Point of Platinum with Junction T₉.
(Commercially Pure 10-Per-Cent. Iridium from J., M. and Co.)

No.	Date.	Observer.	Value found.	Mean of group.
1	September 16, 1904	J. A. H.	1709	—
2	" "	"	1712	—
3	" "	"	1713	—
4	" "	W. H.	1711	1711
5	" "	J. A. H.	1709	—
6	" "	"	1712	—
7	" "	H. C. H. C.	1713	—

VIII.

In Table III (pp. 244—245) are summarised further data regarding the different junctions, which are here grouped according to their composition.

Column I gives the distinguishing number of the junction.

II its composition.

III the diameter of the wires forming the junction.

IV its formula directly obtained by comparison with standards or at fixed points between 400° C. and 1250° C.

V the error of the formula at 0° C.

VI and VII the sensitiveness or "thermoelectric power" of the junction at 400° C. and 1700° C. respectively.

VIII.—Percentage of the t^2 term of the *E.M.F.* at 1700° C. of the whole *E.M.F.* at the same temperature.

IX.—Mean value of the *E.M.F.* in microvolts given by the junction at the melting-point of platinum.

X.—Number of experiments made.

XI.—Mean value given by the junction for the melting-point of platinum in degrees Centigrade.

Junction N. P. L. 3 was part of the stock of 10-per-cent. plat-rhod. alloy obtained from Heräus in 1901. Full particulars regarding junctions N. P. L. 1, 2, and 3 made of this wire are given in the author's paper on high-temperature standards previously alluded to. Some of the observations in the second set included under this heading were made with junction N. P. L. 2, the actual wire used in the direct gas-thermometer comparisons. The three wires coincide to within the limits of accuracy attainable.

T₁₅ is a sample of extremely-carefully prepared wire from Messrs. Johnson, Matthey and Co., made under the personal direction of Mr. George Matthey, F.R.S., to whose kindness the laboratory is indebted for the care spent on the preparation and analysis of a number of specimens of these platinum alloys. Analysis revealed no trace of any other metal present but platinum and rhodium, the figures obtained for these elements being

$$\text{Pt} = 89.9, \quad \text{Rh} = 8.98$$

both being directly determined.

IX.

T₁₄ is a unique specimen in that it consists in what is probably the first wire investigated thermoelectrically, made from the large mass of exceptionally pure platinum-iridium prepared by Mr. Matthey for the construction of the "étalons prototypes" of the kilogramme and metre for the

I.	II.	III.	IV.
No. of junction.	Composition of junction.	Diameter of wires in mm.	Formula for E.M.F. of junction from 400° C. upwards.
N. P. L. 2 and 3 T ₁₅	Pure rhodium alloys— German rhodium 10-per-cent. alloy from Heräus, 1901 Purest English rhodium 10-per- cent. alloy from Johnson, Matthey and Co., 1904	0·62 0·51	$-304 + 8\cdot165t + 0\cdot001663t^2$ $-250 + 7\cdot953t + 0\cdot001842t^2$
M ₄ T ₂₀	Commercial rhodium alloys— Commercial 10-per-cent. rhodium from J., M. and Co., 1903 Ditto, a second sample formerly called T ₆	0·48 0·31	$-692 + 11\cdot55t + 0\cdot001245t^2$ $-446 + 11\cdot697t + 0\cdot001416t^2$
T ₁₄	Pure iridium alloy— Purest English iridium alloy drawn from "étalon" wire, J., M. and Co., 1904	0·54	$-409 + 15\cdot7635t + 0\cdot0007339t^2$
T ₉ M ₃ M ₄	Commercial iridium alloys— 10-per-cent. commercial iridium, J., M. and Co., 1904 Ditto, another sample, 1904..... " " 1903.....	0·33 0·50 0·33	$-442 + 15\cdot6957t + 0\cdot0007349t^2$ $-544 + 15\cdot2403t + 0\cdot001749t^2$ $-781 + 15\cdot5043t + 0\cdot001186t^2$
T ₂₁	Rhodium-platinum against iridio- platinum— Iridium alloy of same sample as T ₉ against rhodium alloy of same sample as T ₂₀ .	0·33 and 0·31	$+4 + 4\cdot0259t - 0\cdot0006809t^2$

International Commission of Weights and Measures in 1886. The analysis made by Stas and by St. Claire Deville of two samples of this alloy gave a mean value

Pt =	89·841
Rh =	0·135
Ru =	0·034
Fe =	0·066
Ir =	9·880
	<hr/>
	99·956

all the constituents being determined directly, and not by difference. This alloy serves as a standard of comparison for all junctions of platinum-iridium wire.

III.

V.	VI.	VII.	VIII.	IX.	X.	XI.
Error of formula at 0° C.	$\frac{dE}{dT}$ at 400° C.	$\frac{dE}{dT}$ at 1700° C.	t^2 term $\times 100$ whole E.M.F. at 1700° C.	Mean value of microvolts at the melting-point of platinum.	No. of experiments.	Mean value of melting-point of platinum in degrees C.
° C.			Per cent.			
-37	9.49	13.82	+ 26	18580	9	1712
-31	9.48	14.21	+ 29	18693	10	1707
-60	12.55	15.78	+ 16	22590	3	1704
-38	12.81	16.61	+ 17	23415	13	1696
-26	16.35	18.25	+ 7	28581	13	1705
-28	16.28	18.19	+ 7	28532	7	1711
-36	16.64	21.18	+ 17	30800	4	1706
-50	16.46	19.52	+ 12	28840	3	1692
+ 1	8.40	1.8	-40	4905	3	1712

T_0 and M_0 are specimens supplied commercially to the laboratory at different dates, the products being stated to be of high commercial purity. M_0 is representative of several alloys of a similar character, not definitely called "pure," but sold simply as 10-per-cent. alloy, the quality of the platinum wire forming the other side of the junction being also unspecified. M_4 and T_{20} are 10-per-cent. rhodium alloys of similar quality bought at different times, and T_{21} is a junction composed of the same alloy of iridium as the sample used in junction T_0 , against the rhodium alloy used in T_{20} . It will be noticed that the sensitiveness of this junction is only about a quarter of that of a pure platinum-rhodium alloy against platinum, and that it *diminishes* fairly rapidly with increase of temperature. In the experiments with this junction the melting-point was taken of a small piece of pure platinum, which was twisted several times round the junction of the two wires. After melting, this formed

into a large drop, which surrounded the point of contact of the two alloy wires.

The specimens of platinum used in making up the junctions were not specially analysed at the laboratory. Five separate samples were utilised. It is, however, certain that the specimens used in the first four junctions and in the experiments with T_{31} were of very high quality, but it was found that the wire used in M_4 and M_5 , when tested thermoelectrically against that of T_{14} and T_{15} , gave an appreciable thermoelectric force at the higher ranges, and it is probably owing to this cause, and not to any lowering of the freezing-point of the platinum by impurities, that the two low values 1692° and 1695° are due.

X.

Rejecting, therefore, these two determinations, the agreement between the remaining seven junctions is of such a character that it appears highly probable that the value 1710° C. represents to within 5° C. the melting-point of platinum as determined by the thermoelectric method.

It may be objected, however, that in spite of the good agreement of determinations made with so many junctions, whose curves of E.M.F. against temperature differ so widely from one another, both as regards slope and degree of curvature, the extrapolation of a formula, which is only known to hold over a range of about 800° C., to cover an additional 500° C., is unjustifiable, and that it is quite possible an intermediate point on the extrapolated part of the curves might not show such good agreement.

XI.

It was, therefore, decided to determine the freezing-point of nickel with some of the junctions as control. Table IV gives the result of these determinations summarised. The nickel used was a very pure sample of nickel berries from Brunner, Mond and Co., made by the Mond process and found by analyses made at the laboratory by Dr. Carpenter to contain 99.6 per cent. nickel before fusion. Three careful experiments made in an electric furnace in a reducing atmosphere by the ordinary crucible method with junction N. P. L. 2. gave 1428° , 1429° , and 1427° C.; a previous determination made on the same material by Dr. Carpenter on a much larger scale, using a wind furnace and a junction from the same stock of wire as T_9 , gave 1427° C. as the temperature of the commencement of solidification. In both these determinations the junctions were protected by thin fire-clay tubes. The two perfectly independent results agree within far less than the probable error.

Some further observations showed that it was quite easy to obtain a well-

defined melting-point of a small granule of nickel round which the junction was wrapped, without sensible oxidation of the metal, in the new type of furnace used for the platinum points. Preliminary experiments with different conditions of immersion, etc., showed that the melting-point thus obtained agreed satisfactorily with the standard method even when no special gas was passed through the furnace, and that any nickel volatilised or diffused into the thermo-junction wires only affected these for a few millimetres of their length over the part actually in contact with the metal. The results obtained with the six junctions used are shown in Table IV.

XII.

It will be noticed that the junction T_{30} , which reads 14° C. low at the platinum point is low by a similar amount at the nickel point, but that the first four junctions given in the table agree fairly well, those which are low at the platinum point being also low near 1400° C.

These data furnish an answer to the possible objection which might be urged against the method that the comparative agreement at 1700° C. is really fortuitous.

Table IV.—Melting-Points of Nickel and Platinum Compared.

(Most probable value for nickel $1427^{\circ} \pm 3^{\circ}$ C., for platinum $1710^{\circ} \pm 5^{\circ}$ C.)

No. of junction.	Date of experiments.	No. of experiments on nickel.	Mean value.	Divergence from probable value.	Platinum point on same junction.	Divergence from probable value.
N. P. L. 3	1905— January 25, J. A. H.....	3	1428	+ 1	1712	+ 2
T_9	1904— November 21, H. C. H. C. (crucible method)	1	1427	+ 0	1711	+ 1
T_{15}	1905— January 28.....	2	1420	— 7	1707	— 3
T_{14}	" 28.....	5	1422	— 5	1705	— 5
T_{30}	" 31.....	4	1412	— 15	1696	— 14
T_{21}	February 6.....	5	1419	— 8	1712	+ 2

The value given by these experiments for the melting-point of platinum,

$$1710^{\circ} \pm 5^{\circ} \text{ C.},$$

is very considerably lower than the previously accepted numbers. Of these earlier determinations undoubtedly the most important is the one made by Violle, which was a calorimetric estimation, depending on the extrapolation of a value determined for the specific heat of platinum from 1200° C. upwards. Violle's value is usually given as 1780° C. In his own memoir he says that

if this value is in error it will probably be found to be too high, as platinum is a metal which softens gradually, and when in this state the specific heat will probably be intermediate between that of the solid and the liquid, thus leading to an error in this direction.

XIII.

A few further words may be said regarding the furnaces, one type of which is here described. Preparations are now being made for building them on a much larger scale, and it is hoped to publish shortly a further account of their construction and uses. In addition to their use for work such as is here detailed, the type of furnace appears to be capable of numerous applications, both scientific and technical.

Of the scientific applications might be mentioned its use in the determination, at steady high temperatures in the absence of noxious gases, of the general physical properties of bodies, such as their coefficient of expansion, density, and specific heat in both liquid and solid states, and also vapour density and dissociation. A horizontal form could easily be arranged for softening and annealing of long lengths of continuous wires, particularly such as cannot be directly heated electrically by current.

It is quite easy to arrange such a furnace to work *in vacuo*, and in this form it might be of use in many chemical investigations. In the preparation of metals like silver for such work as the determination of its electro-chemical equivalent, where the highest possible purity of the product is desirable, it would be quite easy, with an appropriate form of furnace, to refine by distillation considerable quantities of material, as was done by Stas in his classic researches.

The method of distillation in the oxyhydrogen blast employed by Stas suffers from an obvious disadvantage in that he says, after describing the process—"Je dois avouer toutefois que dans les opérations que je viens de décrire *la moitié au moins* de l'argent employé a été perdue." In addition to avoiding this great loss of material, the liability of the metal to occlude gases would in the new furnace probably be much diminished.

For work on radiation, and as a "black body," some rough preliminary experiments have shown the great advantages of this type of furnace over the carbon tube type, which lasts only a very short time, takes a very large current, and gives off large quantities of poisonous carbonic oxide gas.

For the realisation of the Violle Standard of light, in which the unit is the amount of light given off by 1 sq. cm. of pure platinum at its freezing-point, it is likely a furnace of this type might be very convenient, since it might easily be designed to render possible the desired result with a much

smaller quantity of platinum than has hitherto been thought necessary, and at the same time greatly increase the time of solidification, the only period in each experiment during which measurements can be made.

XIV.

In conclusion, I have to thank Mr. Swinburne for several suggestions made at the beginning of the work; Sir William Crookes for kindly replying to queries, and for sending valuable references to the chemical literature of the rare earths forming the tubes; my friends, Mr. R. S. Hutton, lecturer in electro-chemistry at the Manchester University, for references to the American literature, Mr. Sheppard, of the British Nernst Light, Limited, for advice on practical points, and especially Mr. Maurice Solomon, for placing at my disposal valuable knowledge gained in his experience of Nernst filament making. Thanks are also due to Mr. G. Matthey, F.R.S., who provided the very pure metals and alloys used as thermo-junctions; and to the Director of the laboratory for provision of special facilities for this research, including the addition to the thermometric department of a specially-designed switch-board and safe regulating resistances for the 250 and 500-volt circuit of the local electric supply.

A list of the more important references, to work on electrolytic conductivity and furnaces, and to earlier determinations of the melting-point of platinum, is given below.

XV.

LIST OF REFERENCES TO WORK ON SOLID ELECTROLYTES.

- Jablochkoff in 1877 showed that half-baked kaolin conducts when hot.
- Nernst. British Patent, No. 19424. 1897. A minute hollow cylinder of burnt magnesia will run as a lamp.
- Nernst. British Patent, No. 6135. 1898. Deals with differences in behaviour of pure materials and mixtures as lamp filaments. Pure magnesia only works with great difficulty. Best materials for permanence at very high temperatures are zirconia and oxides of the zirconia group.
- Nernst and Wild. 'Zeitschrift für Electrochemie,' vol. 7, p. 273, December, 1900. "Efficiencies of Various Mixtures as Filaments."
- Potter. American Patents, Nos. 652,640 (1900), 715,505 (1902), 719,507 (1903).
- Nernst. 'Göttinger Nachrichten,' 1903, vol. 2, alludes to an attempt to use tubes of solid electrolytic conductors as a furnace for vapour density determinations. He discards these in favour of the iridium tube furnace described.
- Nernst. 'Zeitschrift für Electrochemie,' vol. 9, p. 622. Fuller description of same work.
- Reynolds. 'Göttingen Dissertation,' 1903. "Resistance of Solid Electrolytes at High Temperatures."

LITERATURE OF MELTING-POINT OF PLATINUM.

Vielle. 'Comptes Rendus,' vol. 85, p. 543, and vol. 92, p. 866, 1881, gives 1775° and 1779° C. as determinations made by his calorimetric method.

Holborn and Wien. 'Wied. Annalen,' vol. 47, p. 107, 1892, and vol. 56, p. 360, by thermo-electric method obtain 1780°.

Nernst. 'Physikalische Zeitschrift,' vol. 4, p. 733, 1903, and 'Wied. Ann. Beiblätter,' vol. 25, p. 686. Obtains by an optical method 1782° as melting-point of platinum in iridium tube furnace.

Older determinations by Becquerel, Van der Weyde, etc., vary between 1400° and 2200° C.

The Atomic Weight of Chlorine: an Attempt to Determine the Equivalent of Chlorine by Direct Burning with Hydrogen.

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(Received May 3,—Read May 18, 1905.)

(Abstract.)

Although the atomic weight of chlorine has been determined by Stas and other chemists with extraordinary care, nevertheless owing to the very indirect methods hitherto used in making the comparison between chlorine and hydrogen, it is possible that a constant error may occur in some link of the long chain of connecting ratios. To join up the open ends of the chain by a direct comparison between chlorine and hydrogen, if it could be done with reasonable accuracy, would serve not only to detect any such systematic error, but would permit the accidental errors to be distributed and prevent their accumulation at the unconnected end. According to Professor F. W. Clarke the accumulated "probable error" in his recalculated value for chlorine amounts to ± 0.0048 ; the probable error of the mean of our nine determinations is less than ± 0.002 .

It was at the suggestion of Professor E. W. Morley, of Cleveland, U.S.A., that we have attempted this direct comparison by determining the weight of hydrogen which burns in a known weight of chlorine.

Our method was briefly as follows:—

Chlorine prepared by the electrolysis of fused silver chloride (with purified carbon poles in a Jena glass vessel) was condensed and weighed as a liquid in a sealed glass bulb. This was attached to a vacuum "combustion globe" and the chlorine allowed to evaporate slowly into the globe. The hydrogen prepared by the electrolysis of barium hydrate solution was dried and then absorbed by palladium in a weighed vessel. The palladium, on being warmed, gave off the hydrogen, which was ignited by a spark and burnt at a jet in the

combustion globe previously filled with chlorine. The gases were regulated so as to maintain the hydrogen flame until nearly all the chlorine had been combined; then the palladium was allowed to cool and the hydrogen was turned off just before the flame died out. The hydrogen chloride, as it was formed in the flame, was dissolved by water standing in the globe, which was kept cool by ice. A little hydrogen chloride was formed by the action of the water-vapour on the chlorine in the flame, a corresponding amount of oxygen being liberated. This oxygen was determined in the analysis of the residual gases, which contained, besides traces of air, the small quantity of hydrogen which filled the capillary tube between the tap and the jet when the flame was extinguished, and any that might escape unburnt from the flame. The chlorine remaining unburnt in the globe was about 2 per cent. of that burnt. This unburnt chlorine, as gas and in solution, was determined by breaking thin glass bulbs containing potassium iodide. The residual gases having been pumped out (and any iodine vapour caught by a wash-bottle), the liberated iodine was determined by standard thiosulphate in an atmosphere of carbon dioxide. In the calculation of the unburnt chlorine the atomic weight of chlorine was assumed to be 35.195, and the atomic weight of iodine 126.015.

In each experiment we burnt between 11 and 13 litres of each gas.

The balance, by Oertling, was fixed on a stone pedestal in an underground cellar. The vibrations of the pointer were read by a telescope, Gauss' method of reversals being used. The chlorine and hydrogen bulbs were counterpoised on the balance by bulbs of the same glass and of nearly the same displacement, and the small weights employed in the weighings were reduced to a vacuum standard.

The following were the corrected weights of hydrogen and of chlorine burnt in the several experiments:—

	Hydrogen burnt, in grammes.	Chlorine burnt, in grammes.	Chlorine combined with unit weight of hydrogen.
1.	0.9993	35.1666	35.191
2.	1.0218	35.9621	35.195
3.	0.9960	35.0662	35.207
4.	1.0243	36.0403	35.185
5.	1.0060	35.4144	35.203
6.	0.9887	34.8005	35.198
7.	1.0159	35.7639	35.204
8.	1.1134	39.1736	35.184
9.	1.0132	35.6527	35.188
Mean ...			35.195 ± 0.0019

In the whole of these nine experiments 9·1786 grammes of hydrogen combined with 323·0403 grammes of chlorine, hence the equivalent weight of chlorine, calculated in mass, is 35·195.

The number we have obtained for the atomic weight of chlorine is appreciably higher than that calculated by F. W. Clarke from the previous determinations, and is slightly higher than Stas' value :—

Clarke's calculation.	Stas.	Dixon and Edgar.	
35·179	35·189	35·195	H = 1
35·447	35·457	35·463	O = 16

Since our experiments were completed we have heard that Professor T. W. Richards is engaged on a revision of Stas' work on the composition of silver chloride. G. P. Baxter quotes the value 35·467 as being obtained by Richards and Wells for the atomic weight of chlorine—a number slightly higher than ours.

Thorianite, a New Mineral from Ceylon.

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(Received May 1,—Read May 18, 1905.)

The mineral which forms the subject of this paper was collected in Ceylon during the progress of the mineral survey of the island, which was commenced in 1903 under Professor Dunstan's supervision, with the principal object of determining the extent to which economic minerals, such as graphite, mica, etc., occur, and if possible of discovering other minerals of commercial importance. The minerals collected by Mr. A. K. Coomaraswamy and Mr. James Parsons, the officers entrusted with the survey in Ceylon, are submitted to examination and analysis in the Scientific and Technical Department of the Imperial Institute, and are subsequently subjected to such technical trials as may be necessary in order to ascertain their precise uses and to determine their value.

Among the materials thus received from Ceylon at the Imperial Institute was a small quantity of a heavy black mineral occurring chiefly in small roughly cubical crystals. This mineral was, in the first instance, furnished to the officers of the mineral survey by Mr. W. D. Holland, who believed it to be uraninite or pitchblende. He had previously sent specimens to several persons in this country under this name.

A chemical examination of the small specimen received at the Imperial Institute showed, however, that the mineral contained a large proportion of thorium in the form of the dioxide (thoria) and only a small proportion of uranium. It was evident that this was a new mineral chiefly composed of uncombined thoria (ThO_2). Pending the arrival of more material to enable a further examination of its properties to be made, a preliminary account of its composition and properties was communicated by one of us to 'Nature,'* and the name *thorianite* was suggested for the substance, which contained at least 75 per cent. of thoria.

It was also stated that the mineral was radio-active and that it apparently contained helium, points which would be made the subject of further investigation.

The publication of these results was followed by a communication to 'Nature'† from Sir W. Ramsay, who announced that he had purchased 6 cwt.

* March 30, 1904, p. 510.

† April 7, 1904, p. 533.

of the mineral from Mr. Holland some months previously and had been engaged in its examination. He was unable to confirm the statement that it contained thoria, but announced that it had furnished considerable quantities of helium. In a second communication to 'Nature'* Sir W. Ramsay modified the statement he had previously made that the mineral contained practically no thorium.

Further small supplies of the mineral having since been received at the Imperial Institute, we have been enabled to confirm the conclusion first arrived at that the substance is chiefly composed of thoria, and we now desire to bring before the Royal Society an account of this remarkable new mineral for which the name thorianite is appropriate.

A general account of the composition, properties, and uses of thorianite is included in Professor Dunstan's official 'Reports on the Results of the Mineral Survey in Ceylon, 1903-4,' which was issued as a Parliamentary Paper (Cd. 2341) in January, 1905.

Occurrence of Thorianite in Ceylon.

The following account of the occurrence of the mineral, at first supposed to be "uraninite," has been given in official reports by Mr. A. K. Coomaraswamy, B.Sc., the Director of the Mineral Survey in Ceylon.

"Mr. Holland of Dikmukulana has for long taken an interest in local mineralogy, amongst other things obtaining specimens of 'nampu' (gem-bearing gravels) from as many localities as possible by offering a small reward to the native 'gemmers' who bring it. It is difficult to persuade the native that gems are not required or to get him to reveal the true source of 'nampu.' These difficulties overcome, the examination of 'nampus' is an ideal method of gaining a knowledge of heavy minerals of any district. Early in 1903 Mr. Holland obtained 'uraninite' amongst his samples and was gradually able to get as much as 6 cwt. brought to him along with other stuff. This material was sent to England and sold to Sir W. Ramsay at the rate of £50 for 6 cwt. Subsequently Mr. Holland induced a native to show him the source of the material, and finding that some quantity occurred, he took out a prospecting license in the full belief that the locality was Crown land.

"Thorianite, together with a mineral regarded as thorite, and a number of other heavy minerals, is found near Kondurugala, Bambarabotuwa, Province of Sabaragamuwa. The principal deposit occurs in and near the bed of the upper part of the Kuda Pandi-oya, a small stream, which at first occupying a small north-west and south-east strike valley north of the Hopewell-Hapugastenna bridle path, turns through nearly a right angle and joins the Maha Pandi-oya a little below the same path. In the bed of the Kuda Pandi-oya, and in a small 'deniya' swamp just below the swamp, the thorianite is to be obtained in considerable abundance. It could not be discovered *in situ*, but it can hardly be doubted that it is derived from some rock outcropping not far distant from the highest part of the little

* April 14, 1904, p. 559.

stream; the stream is so small that after a few days of drought (not very usual in this wet district) no running water is met with above the camp. The matrix is no doubt a rock of granitic type similar to those containing zircon, allanite, etc., which have been met with elsewhere in the Balangoda district, intrusive in the Charnockite series, and classed as belonging to the Balangoda group. Of these rocks the largest exposure (a narrow lenticular mass two miles or more in length) is that of zircon granite on Massena estate (six miles);* the rock consists of feldspars, quartz, biotite, zircon, and ilmenite; smaller exposures of zircon granite are found on Herimitigala (eight miles) and Hopewell estates (15 miles); at Denegama bridge, on the road between Balangoda and Belihul-oya, and near the 91st milepost on the same road. There are also similar granites without accessory minerals exposed—e.g., on the main road about a mile below Balangoda. The allanite-granite, or pegmatite, is best seen on Lower Denegama estate, where it occurs as a dyke 3 or 4 feet thick, forming a conspicuous ledge in the bed of the stream which runs through that part of the estate. The rock is composed of feldspars (chiefly orthoclase), quartz, biotite, and allanite. The allanite forms thin tubular idiomorphic and larger irregular crystals, the biggest having a greatest diameter of 3 inches. Almost identical rocks occur (1) in the Weweldola on Dikmukulana estate (11 miles), and (2) at Weligepola (9 miles). It is important to observe that a pegmatite rock, composed mainly of pink orthoclase, quartz, and biotite, with accessory apatite, tourmaline, ilmenite, etc., has been observed on Ambalawa estate, Gampola,† containing, in addition to the above-named minerals, a few cubic crystals of a black mineral at first regarded as uraninite, but which is almost certainly thorianite.

"To return to the Kondurugala locality, the thorianite is probably derived from a granitic rock with no very large outcrop, but in which it occurs in considerable abundance; perhaps together with the zircon, thorite and ilmenite, which quite possibly, however, occur separately in other rocks of a similar character. The outcrop of this rock could not be discovered owing to the dense jungle and thick soil and landslips; rock (mainly decomposed granulite) is indeed exposed at several points in the beds of the Kuda Pandi-oya and of the small streams joining it, but any search for the outcrop of a particular rock in the adjoining jungle could only be expected to succeed at the cost of a large expenditure of time and money, and might even then result in failure.

"There is a large area, including at least the whole of Sabaragamuwa and parts of the central, western, and southern provinces, wherein this or other rare heavy minerals may be looked for.

"It is unlikely that any very extensive deposit of any of these rare heavy minerals will be found, but they may be expected to occur at various points in moderate amounts. In the Kuda Pandi-oya valley a total of 5 tons might, perhaps, be obtained; from the Alupola-dola or the Kuda-oya I doubt if half a ton could be profitably extracted, but these estimates are quite uncertain. The Gampola occurrence is quite without commercial value. The total amount actually obtained in Bambarabotuwa, so far, does not exceed 15 cwts. In the

* The distances are quoted from Balangoda.

† '*Spolia Zeylanica*,' vol. 1, part iv, 1904.

immediate neighbourhood of Kondurugala the Walaweduwa jungle seems the most favourable district for investigation. An examination of the Ratganga valley towards the west showed that thorianite is absent there, and that even zircon is very scarce; but on the north-east one or two heavy minerals not yet determined were actually obtained in the southern part of the Walaweduwa Crown Forest Reserve, and further work on that side of Kondurugala might be useful. It must be mentioned, however, that the district is a very wet one, the jungles swarming with leeches; it is also very inaccessible, provisions and camping effects having to be carried fully 20 miles from Balangoda. Camping in these jungles is absolutely useless except in fine weather; and in the absence of a detailed map observations cannot be very accurately set down.

"Since August, 1904, a small deposit of the mineral provisionally identified as thorite was discovered at Durayakanda, South of Gilimale, about six miles from Ratnapura.

"A further amount of 1,200 lb. of thorianite has since been obtained from Bambarabotuwa."

Description of Thorianite.

Thorianite, as it occurs naturally, is often associated with other minerals, and is not easy to obtain in a completely separate condition.

Dr. J. W. Evans has made a preliminary examination of the crystallographic characters, and intends to further study this subject. It may be stated now that the mineral occurs in small cube-like crystals up to nearly a centimetre in diameter, the largest, so far seen, measuring rather more than 8 mm. In most specimens the colour is a dull grey or slightly brownish black, but those crystals which have not suffered from attrition in the streams are a jet black with a bright resinous or pitchy lustre. The difference may be attributed partly to the grinding of the surface, and partly to superficial chemical changes. The mineral thus differs from uraninite or pitchblende which usually occurs massive, and not obviously crystalline. The streak furnished by uraninite is brown with a tinge of green.

By transmitted light the mineral is opaque except in thin sections.

The double refraction is very low. The refractive index probably exceeds 1.8.

The only faces that are ordinarily developed on the crystals of thorianite are apparently those of the cube. These have a very uneven surface, especially in specimens that have not suffered much from attrition or alteration. This character of the surface is mainly the result of the development of a number of small vicinal faces. In some cases larger faces of similar character are present, meeting at very obtuse re-entrant or salient angles, and reminding one of those seen in some crystals of fluorspar. In other crystals the faces show a more or less irregular curvature.

The indefinite character of the surface prevents any accurate determination of the angles. The goniometric readings vary 2 or 3 degrees on either side of 90 degrees, according to the portions of the surface from which the image is reflected, but there is in most cases no satisfactory evidence that the faces as a whole are not virtually at right angles. Some crystals, however, appear to be distorted and have angles differing from a right angle by as much as 5 degrees or even more.

Occasionally twin crystals are met with and these are of some interest. They are interpenetrant twins on a face of the octahedron as twinning plane, and one of the diagonals of the cube as twinning axis, exactly similar to those of fluorspar. As in the case of that mineral the coigns of one cube project as pyramids on an isosceles triangular base on the face of the other. Sometimes the compound form is almost completely regular, four edges of each cube meeting at one point or approximately so at both ends of the common diagonal that forms the twinning axis; at other times the composition is more irregular, and a number of coigns project from the faces of a cube in such a manner that though the faces of one coign are parallel to those of another, they are not in the same plane. In these forms the twinning axis and plane are the same for all the coigns, even when there is more than one projecting from the same face, the more acute point of the pyramid pointing to the coign of the cube from which the twinning axis emerges. The diagonal which constitutes this axis has therefore crystallographic characters different from those of the other three diagonals, about which this twinning cannot apparently take place, and the symmetry of the crystal must be considered as rather rhombohedral than cubic, although the angles are apparently right angles. The same considerations would apply to fluorspar, in which case the essentially rhombohedral character of its symmetry is confirmed by the occurrence of crystals in which only those faces of the four-faced cube or tetrakis hexahedron $\{310\}$ are developed, in which the finite intercepts are of opposite signs. These faces may be represented by the symbol $\{3\bar{1}0\}$, and are those which bevel the edges that do not pass through the coigns at the ends of the unique diagonal. They together form a scalenohedron, which is in fact the scalenohedron $\{13\bar{4}2\}$ of the rhombohedral system, assuming the cube as the fundamental rhombohedron.*

A similar scalenohedron $\{2\bar{1}0\}$ or $\{12\bar{3}1\}$ is repeatedly met with in crystals of halite.†

* 'Lehrbuch der reinen und angewandten Krystallographie,' 1830, p. 178, fig. 572.

† F. von Kobell, "Über Merkwürdige Krystalle von Steinsalz," 'Journal für praktische Chemie,' 1861, vol. 84, p. 420; K. Andrée, "Über Steinsalz Krystalle von hexagonal-rhomboëdrischer Pseudosymmetrie aus Sicilien," 'Centralb. für Mineralogie,' etc., 1904, p. 88.

It is interesting to notice that chabazite, which is cubic in general appearance, but really rhombohedral, having its angles differing from right angles by nearly 5 degrees, twins in exactly the same manner as fluorspar and thorianite.

The inference that thorianite is essentially rhombohedral in character is confirmed by the observation that in sections cut perpendicular to the twinning axis, the substance is practically isotropic.

Thorianite shows no definite cleavage, but the mineral is traversed by irregular cracks which appear to follow the direction of the basal plane more frequently than any other. On fracture, it shows an irregular surface, which is more or less conchoidal on a small scale.

The hardness of the mineral is nearly 7, which distinguishes it at once from uraninite with a hardness of 5.5.

Under the blow-pipe thorianite is infusible. It decrepitates, and if raised to a sufficiently high temperature, is highly incandescent.

It is sometimes associated in rolled fragments with a smooth, yellow-brown, apparently amorphous material, of hardness 6, which envelopes it or forms a rounded deposit on its faces. This substance is reddish-yellow in colour when viewed in thin sections by transmitted light. Zircon also sometimes occurs intergrown with thorianite.

The density of different specimens of thorianite varies between 8 to 9.5 and 9.7. The higher numbers probably represent the density of the actual mineral, which in some cases exhibits cavities partially filled with a yellow ochreous material and also inclusions of zircon, one of the minerals generally associated with thorianite, and these associated minerals, especially those which contain thorium, will be investigated if a sufficient quantity can be obtained separated from thorianite.

The mineral is easily powdered and then dissolves readily in strong nitric acid or in diluted sulphuric acid, with evolution of a gas which is chiefly helium. Thorianite is scarcely attacked by hydrochloric acid.

Thorianite is highly radio-active, and, in fact, may prove to be one of the most radio-active of minerals. The cause of this radio-activity is referred to below.

Composition of Thorianite.

The methods used in determining the composition of thorianite are founded on those suggested by Glaser*, Meyer and Marckwald†, Fresenius and Hintze‡, and Benz§.

* 'Zeits. Anal. Chem.,' 1897, vol. 36, p. 213.

† 'Ber.,' 1900, vol. 33, p. 3003.

‡ 'Zeits. Anal. Chem.,' vol. 35, p. 343.

§ 'Zeits. Ang. Chem.,' 1902, p. 297.

The results are shown in the table on p. 261, which includes the data obtained from three separate specimens, numbered I, II, and III.

In the estimation of the metals, 2 grammes of the finely powdered mineral were dissolved in about 15 c.c. of nitric acid of specific gravity 1.4, and after decomposition was complete the solution was diluted and filtered. The insoluble residues in specimens II and III were very small, and were treated with hydrofluoric acid to estimate silica. In I the residue chiefly consisted of zircon which was fused with potassium hydrogen sulphate to extract zirconia, and the residue treated as before with hydrofluoric acid to estimate silica. Except for this associated zircon, no zirconia was found in the mineral.

The acid filtrate from the insoluble residue was diluted to about 300 c.c. and 5 c.c. of hydrochloric acid added. Hydrogen sulphide was then passed through the liquid to precipitate lead which was finally weighed as sulphate. The filtrate was boiled to remove hydrogen sulphide, and oxidation of the last traces of this substance effected with bromine water. To the hot acid solution, amounting to about 350 c.c., excess of ammonium oxalate was added, and the precipitate of oxalates of thorium and cerium, etc., allowed to settle overnight and then filtered. The filtrate was evaporated to dryness and treated with nitric acid to destroy oxalic acid, and diluted with water. The calcium and magnesium were separated from other metals by precipitating the latter with ammonia and ammonium chloride. This precipitate was dissolved in hydrochloric acid, excess of acid neutralised, and the solution diluted to 500 c.c. A few drops of solution of sodium sulphite were added, and the liquid boiled to precipitate any titanous acid. No titanium was, however, present. The liquid was evaporated, and the iron oxidised with a few drops of nitric acid. The liquid was neutralised with a few drops of ammonia, and finally excess of ammonium carbonate added. The carbonates first precipitated were re-dissolved on further addition of the reagents, showing the absence of alumina. The iron was separated as sulphide. The filtrate was boiled, acidified with hydrochloric acid, and again boiled to remove all the carbon dioxide. The uranium in solution was precipitated with ammonia, and finally weighed as urano-uranic oxide U_3O_8 .

The precipitate containing the oxalates of thorium and cerium, etc., was dried, and the oxalates were then decomposed by nitric acid, and the metals obtained in solution as nitrates. After diluting to 250 c.c., sodium thio-sulphate was added to the slightly acid boiling liquid till no further precipitate of thorium salt was obtained. The liquid was boiled for a short time, the precipitate filtered off and dissolved in hydrochloric acid, and the

operation twice repeated to completely separate the cerium. To the united filtrates ammonia was added, and the precipitate of hydroxides of the cerium, etc., containing a little thorium and any yttrium present, was dissolved in hydrochloric acid, and the trace of thorium precipitated as above described from a small bulk of liquid. The thorium precipitates were dissolved in hydrochloric acid, and the thorium re-precipitated as hydroxide and finally weighed as the dioxide ThO_2 . The filtrate from precipitation of the cerium earths with ammonia contains lime if such were present in the original mineral. This was separated as oxalate and weighed as oxide.

Determinations of the equivalent of thorium made with the precipitated dioxide obtained in the course of the analysis of the third specimen (see p. 261) by conversion into the sulphate gave 57·25, corresponding with an atomic weight of 229. The accepted atomic weight of thorium, relative to hydrogen taken as 1, is 230·8.

The solution from which thorium had been thus removed, containing cerium and the associated earths, including any yttrium, was treated with ammonia; the precipitate dissolved in dilute sulphuric acid, and the solution, after neutralisation, saturated with potassium sulphate. No yttrium was found in the filtrate by dilution and addition of ammonia.

The double sulphates of potassium with cerium, and of the associated metals lanthanum and didydim, were warmed with ammonia solution, by which means the earths were obtained as hydroxides. These were dissolved in hydrochloric acid and re-precipitated by potash solution. The hydroxides were washed by decantation, a little potash solution added, and chlorine gas passed until the liquid was saturated. The lemon-coloured hydrated ceric oxide was filtered off, re-dissolved, and re-precipitated as hydroxide, and the cerium weighed as the dioxide CeO_2 . The filtrate containing lanthanum and so-called didymium was acidified with hydrochloric acid, boiled to remove chlorine, and the earths precipitated with ammonia and weighed as the oxides.

The uranous oxide (UO_2) was separately estimated by Hillebrand's method as follows:—One or 2 grammes of finely powdered mineral were introduced into a stout tube together with 20 to 30 c.c. of dilute sulphuric acid, consisting of one part of acid to five parts of water. The air was then displaced by carbon dioxide, the tube sealed off, and then heated to 180°C . for several hours till decomposition was complete. The solution obtained was diluted with recently boiled water, and the uranous sulphate titrated with potassium permanganate.

The method adopted for the determination of helium and associated gases consisted in decomposing the mineral by means of dilute sulphuric acid

consisting of one part of acid to five parts of water.* Ten grammes of the powdered mineral were used, and the gas collected in a gas burette over mercury with the usual precautions. The mixture was heated at 100°. Decomposition at this temperature was almost complete in one day, but the experiment was allowed to continue for two days to ensure the liberation of all the gas.

The gas collected amounted to 105 c.c. at standard temperature and pressure, which corresponds to 10·5 c.c. of gas, chiefly helium, from one gramme of thorianite.

Analyses of Thorianite.

	I. Per cent.	II. Per cent.	III. Per cent.
Soluble in nitric acid—			
Thorium dioxide	72·24	76·22	78·86
Uranium „	11·19	12·33	6·03
Uranium trioxide	—	—	9·07
Cerium dioxide.....	6·39	8·04	1·02
Lanthanum and didymium oxides ...	0·51		
Yttrium oxide	—	—	—
Lead „	2·25	2·87	2·59
Ferric „	1·92	0·35	0·46
Calcium „	—	—	1·13
Helium	—	—	0·39†
Titanium dioxide	—	—	—
Phosphoric oxide	—	—	trace
Insoluble in nitric acid—			
Zirconium oxide	3·68	—	} 0·20
Silica	1·34	0·12	
Residue from fusion with potassium			
hydrogen sulphate	0·41	—	—

Of the three specimens of thorianite analysed the first was too small to admit of any treatment to separate associated minerals, and proved to contain associated zircon. Specimens II and III were separated as far as possible from extraneous minerals, and represent a nearer approach to the single mineral. The highest amount of thoria yet found is nearly 79 per cent., which shows that thorianite is the richest mineral in thoria at present known.

* Hillebrand, *loc. cit.*

† If the whole of the gas is calculated as helium.

Constitution of Thorianite.

From the analytical results, it will be seen that the constituents other than thoria show, as was to be expected in a mineral of this character, some variation. In Nos. I and II cerium dioxide occurs up to the extent of 8 per cent., while in No. III it becomes almost insignificant. The uranium appears to occur in the condition of both uranous and uranic oxides. It is, however, intended to further investigate this question, since the presence of uranic ochre on the surface of some specimens would indicate that the mineral may have suffered considerable superficial oxidation, and that crystals may be found containing a much smaller proportion of uranic oxide. Of the other oxides present, zirconia in the insoluble residue may be safely classed as an impurity arising from zircons which are invariably found with thorianite, sometimes included within the crystalline thorianite. Silica and ferric oxide may be neglected as contaminations. Leaving out of consideration for the present the oxides of lead and calcium (not a constant constituent) the mineral consists of a large amount of oxide of thorium and a small amount of oxides of uranium, with a smaller and variable amount of cerium oxide, the precise significance of which is at present doubtful.

In the original condition the uranium may have existed entirely as dioxide. There can be little doubt that the dioxides of thorium and uranium, as well as certain of the salts of these metals, are isomorphous. In nature these oxides have not been found in a pure crystalline state, but crystals of each have been obtained artificially. Crystalline thoria was obtained by Troost and Aouvrard* whilst studying the relation between the double phosphate of potassium and thorium and that of potassium and zirconium. The phosphates were first obtained by adding to fused potassium orthophosphate, thoria, thorium phosphate or anhydrous thorium chloride. On raising the double phosphate to such a temperature that both alkali and phosphoric acid were volatilised, thoria was obtained in crystals belonging to the cubic system; the cuboctahedron and rhombic dodecahedron being the forms observed.† Again, uranium oxide was first obtained in an octahedral form by Wohler by heating a mixture of uranium oxychloride with sodium chloride and ammonium chloride.‡ Later, Hillebrand repeated the experiment, and obtained practically pure uranium dioxide in black octahedral crystals of a specific gravity of about 11.§

The hydrate of thorium sulphate $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ is also, according to

* 'Comptes Rendus,' 1886, vol. 102, p. 1422.

† *Loc. cit.*

‡ 'Liebig's Annalen,' 1842, vol. 41, p. 345.

§ 'Zeitschrift für Anorg. Chemie,' 1893, vol. 3, p. 243.

Rammelsberg,* monoclinic in crystalline form and isomorphous with the corresponding hydrate of the uranium salt $U(SO_4)_2 \cdot 9H_2O$.

Our analyses of different specimens of thorianite are hardly sufficiently numerous to enable us to conclude that the oxides of thorium and uranium bear a definite relation to one another in the mineral. It seems probable that the mineral belongs to the class of substances known as isomorphous mixtures of which the simple form would be represented by the formula XO_2 , where X represents a tetravalent element the dioxide of which crystallises in the isometric system the extremes of which would be UO_2 and ThO_2 .

Thorianite is evidently closely related to uraninite (pitchblende) in constitution. The crystalline form of the two minerals is the same and the constituents of both are similar. Hillebrand's analysis of the Branchville varieties of uraninite, which were stated to be nearly unoxidised, furnished 72.25 per cent. of uranium dioxide and only 13.27 of uranium trioxide.† Uranium dioxide very readily oxidises on exposure to air, and it was only by completely excluding the air that Hillebrand succeeded in obtaining the pure oxide artificially. It is, therefore, certain that the natural varieties of the oxide so far examined must have suffered alteration and oxidation, and that originally their principal constituent was uranium dioxide. Most of the massive varieties of uraninite are very impure, and this may account in a large measure for the presence of many oxides in this mineral which appear to have very little in common with the principal constituents. Lead oxide is apparently generally present in thorianite. It occurs in small amount and may be combined as uranate. In the case of thorianite the crystallographic examination has shown that the mineral has crystallised with difficulty, and that it is more or less contaminated with those minerals which crystallised at the same time, as well as with impurities contained in the magma from which crystallisation occurred.

As far as the present investigation has gone it appears probable that thorianite is isomorphous with uraninite, and that in the thorianite of Ceylon some of the thoria is replaced by the corresponding uranium oxide. The evidence, however, is not sufficient to show whether this is a case of isomorphous mixture, as seems probable, or of true chemical replacement.

It is obvious that the mineral is one of exceptional interest, and that it presents many problems for investigation, among them being the question of the possible occurrence of small quantities of hitherto little known or unknown elements.‡ The material furnishes a satisfactory source of pure

* 'Berl. Acad. Ber., 1886, p. 603.

† 'Amer. Journ. Sci.,' 1890, vol. 40, p. 384.

‡ Since this was written Hahn, in a communication to the Royal Society ('Roy. Soc.

thoria, a fact which is of commercial importance as well as of scientific interest.

We have shown that thorianite is chiefly composed of thoria, as at present understood. Baskerville believes that he has obtained evidence that the substance at present known as thorium is composed of more than one element, and that he has separated thoria into three oxides differing in density, and one of which is little, if at all, radio-active. These conclusions have, however, been called in question by Meyer and Gompertz,* who assert that thoria shows no evidence of being other than a single substance.

Determination of the rate of decay of the radio-activity of thorianite made in Lord Blythwood's Laboratory by Mr. H. S. Allen have shown that this property of the mineral is probably consistent with the thorium, uranium, and small amount of radium present.

The radio-activity of the mineral was measured in a parallel plate apparatus, using sufficient material to entirely cover the lower plate. The observed rate of leak under these conditions was 6900 divisions per minute equivalent to a current through the apparatus of approximately 5.5×10^{-11} ampères. Thorianite is, therefore, somewhat less active than some of the specimens of pitchblende examined by Madame Curie, whose results with this mineral are as follows:—

Pitchblende from Johanngeorgenstadt.....	8.3×10^{-11} ampères	
„ „ Joachimsthal	7.0×10^{-11}	„
„ „ Pzibram.....	6.5×10^{-11}	„
„ „ Cornwall	1.6×10^{-11}	„

A series of measurements of the rate of decay of activity of the emanation from thorianite have been made; 16.5 grammes of the mineral were heated in a hard-glass tube, and the emanation, previously dried over phosphorus pentoxide, collected in the testing vessel. It was set aside for 6 hours in order to allow the thorium emanation to decay, and then measurements of the activity were made daily.

The results showed that during the first four days the rate of decay was greater than that observed by Rutherford for radium emanation, but that after this period the rate of decay of activity became identical with that of radium emanation. It is probable that the greater rate of decay during the first four days was due to the presence of thorium "excited activity" which, Proc., 1905) has announced the existence in thorianite of a small quantity of a new element, which produces the "thorium emanation." This was separated from the 6 cwt. of the mineral referred to earlier in this paper. It must not be overlooked that the consignment, though apparently worked up as a whole, was doubtless a mixture containing several other minerals than thorianite.

* 'Ber.,' 1905, vol. 3, p. 187.

according to Rutherford, decays to half value in the course of 11 hours, whereas the radium emanation falls to half value only in about 3·7 days.

These results clearly indicate the presence of radium emanation in the "total emanation" from thorianite, and that consequently this mineral must contain radium.

Commercial Value of Thorianite.

Owing to the increasing employment of thoria for the manufacture of incandescent gas mantles, the demand for minerals containing thorium has largely increased. The demand is chiefly met from the deposits of sand containing a small percentage of monazite (phosphate of the cerium metals and thorium) which occur in Brazil and in North Carolina. Owing to the foreign control of these sands, British manufacturers have experienced difficulty in manufacturing thorium compounds. Thorianite is, we believe, the first deposit of a thorium mineral to be discovered on British territory. Consignments of thorianite from Ceylon, containing about 70 per cent. of thoria, have been recently sold in this country at the rate of £1500 per ton.

For the manufacture of thorium compounds thorianite possesses the advantage, not shared by any known thorium mineral, of containing uncombined thoria, soluble in nitric acid with formation of thorium nitrate.

The Perturbations of the Bielid Meteors.

By A. M. W. DOWNING, D.Sc., F.R.S.

(Received May 13,—Read June 8, 1905.)

In the calculations, the results of which are embodied in this paper, it is assumed that in the apparition of the Bielid Meteors noted in November, 1885, we have an observation of the main part of the stream. It is also assumed that the periodic time of the stream is $6\frac{1}{2}$ years, as appears to be now the general opinion of the chief authorities on the subject, and which agrees closely with the periodic time found for the associated comet.

On these assumptions we ought again to encounter the central part, or at least a neighbouring segment of the stream, close to the central part, in November of the present year. It accordingly became a matter of interest to determine the perturbations to which the segment of the meteor stream, encountered in November, 1885, has been subjected in the interval, in order to ascertain the possibility or otherwise of an encounter with the same segment next November, especially as it was known that this segment of the stream was in close proximity to Jupiter during 1900-01.*

The tabular statements given below exhibit the results of the calculations of the special perturbations by Jupiter and Saturn in the interval referred to. The perturbations have been determined by the method of Variation of Constants, the adopted interval for quadrature being 40 days, except for the period July, 1900—April, 1902, during which the interval was reduced to 20 days, on account of the proximity of Jupiter.

The adopted position of the radiant point is

$$\alpha = 24\frac{1}{2}^{\circ}, \quad \delta = +43\frac{1}{2}^{\circ},$$

at the epoch, November 27, 1885, 6 h., G.M.T.

The elements of the corresponding osculating ellipse, on the assumption of the periodic time as stated above, and referred to the epoch and mean equinox of November 27, 1885, 6 h., are as follows:—

Mean anomaly	M	355° 30'
Perihelion	π	110 56
Ascending node	Ω	245 43
Inclination	i	13 10
Eccentricity.....	ϕ	49 9 ($e = 0.7564$)
Mean daily motion	n	532'' 20
Semi-axis major	a	3.5423

* Cf. Abellmann, 'Astron. Nachrichten,' No. 3516.

The meteor stream encounters the Earth at the descending node of its orbit. It will be noticed that the motion in the orbit is direct.

It may be pointed out that in this orbit the aphelion distance is 6.2. The meteor stream, therefore, crosses the orbit of Jupiter, the mean distance of which is 5.2, and extends beyond it to about the unit of distance. It does not, however, reach the orbit of Saturn, the mean distance of which is 9.5.

The particulars of the relative positions of the adopted point in the meteor stream with reference to the Sun, and with reference to Jupiter and Saturn, during the interval with which we are concerned, are given in the following table, in which the nomenclature is:—

- v True anomaly of the Bield.
 $\log r$ log of radius vector of the Bield.
 ϵ_1 Angular separation, Bield—Jupiter.
 $\log \rho_1$ log of distance, Bield—Jupiter.
 ϵ_2 Angular separation, Bield—Saturn.
 $\log \rho_2$ log of distance, Bield—Saturn.

Date.	v .	$\log r$.	ϵ_1 .	$\log \rho_1$.	ϵ_2 .	$\log \rho_2$.
1885. Nov. 18	304°	0.03	117°	0.78	38°	0.92
1886. Mar. 18	88	0.17	343	0.62	259	0.97
July 16	124	0.42	316	0.61	226	1.04
Nov. 13	140	0.55	309	0.63	216	1.08
1887. Mar. 13	149	0.63	309	0.64	211	1.11
July 11	156	0.69	311	0.64	206	1.13
Nov. 8	161	0.73	314	0.62	207	1.15
1888. Mar. 7	166	0.76	320	0.59	207	1.16
July 5	170	0.78	324	0.55	207	1.16
Nov. 2	175	0.79	329	0.50	207	1.17
1889. Mar. 2	178	0.79	334	0.43	208	1.17
June 30	182	0.79	340	0.35	209	1.17
Oct. 28	186	0.78	346	0.26	209	1.17
1890. Feb. 25	190	0.77	352	0.16	210	1.16
June 25	194	0.75	358	0.10	210	1.16
Oct. 23	199	0.72	4	0.10	209	1.15
1891. Feb. 20	205	0.68	10	0.16	208	1.14
June 20	212	0.62	14	0.24	206	1.12
Oct. 18	222	0.54	15	0.32	200	1.10
1892. Feb. 15	238	0.39	10	0.42	187	1.07
June 14	284	0.10	335	0.59	146	1.02
Oct. 12	74	0.10	196	0.79	0	0.92
1893. Feb. 9	121	0.39	161	0.86	318	0.90
June 9	138	0.54	154	0.91	305	0.92
Oct. 7	148	0.62	155	0.95	299	0.93
1894. Feb. 4	155	0.68	158	0.99	296	0.94
June 4	161	0.72	163	1.01	294	0.96
Oct. 2	165	0.75	168	1.03	293	0.96
1895. Jan. 30	170	0.77	174	1.04	292	0.97
May 30	174	0.79	180	1.05	292	0.97
Sept. 27	178	0.79	186	1.06	292	0.98
1896. Jan. 25	181	0.79	192	1.06	292	0.98
May 24	185	0.79	198	1.06	292	0.98
Sept. 21	189	0.78	204	1.04	292	0.98

Date.	v .	$\log r$.	ϵ_1 .	$\log \rho_1$.	ϵ_2 .	$\log \rho_2$.
1897. Jan. 19	193°	0·76	209°	1·03	291°	0·98
May 19	196	0·73	214	1·01	290	0·98
Sept. 16	203	0·70	218	0·99	288	0·98
1898. Jan. 14	210	0·64	221	0·96	284	0·99
May 14	218	0·57	221	0·98	290	1·00
Sept. 11	232	0·45	216	0·90	268	1·02
1899. Jan. 9	262	0·22	195	0·85	243	1·04
May 9	32	9·96	75	0·72	117	1·02
Sept. 6	112	0·32	4	0·52	41	0·93
1900. Jan. 4	133	0·50	351	0·37	22	0·86
May 4	145	0·60	349	0·22	14	0·80
Sept. 1	153	0·66	350	0·04	10	0·75
Dec. 30	159	0·71	354	9·85	8	0·70
1901. Apr. 29	164	0·74	358	9·85	6	0·67
Aug. 27	169	0·77	3	0·04	6	0·64
Dec. 25	173	0·78	10	0·21	5	0·62
1902. Apr. 24	177	0·79	17	0·34	5	0·61
Aug. 23	180	0·79	24	0·44	5	0·61
Dec. 20	184	0·79	31	0·52	5	0·62
1903. Apr. 19	188	0·78	38	0·58	5	0·63
Aug. 17	192	0·76	45	0·63	5	0·65
Dec. 15	197	0·74	51	0·66	4	0·68
1904. Apr. 13	202	0·70	57	0·68	2	0·71
Aug. 11	206	0·65	62	0·69	0	0·75
Dec. 9	217	0·58	64	0·68	356	0·79
1905. Apr. 8	230	0·46	62	0·65	346	0·85
Aug. 6	257	0·24	45	0·60	322	0·93
Dec. 4	23	9·93	290	0·68	201	1·02

1885, December. Perihelion passage at end of month.

1890, August. Conjunction with Jupiter at beginning of month.

1892, August. Perihelion passage at end of month.

1899, April. Perihelion passage.

1901, February. Nearest approach to Jupiter at end of month ; distance
= 0·644.

1905, November. Perihelion passage on 20th.

The next table gives the computed values of the perturbations of each element of the initial osculating ellipse at certain intervals during the period considered, and the concluded elements for the epoch, November 14, 1905, 0 h., G.M.T.

The masses of Jupiter and Saturn adopted in the calculations are respectively:—

Jupiter 1 : 1047·35 ; Saturn 1 : 3501·6.

The effects of the approaches to Jupiter in August, 1890 (distance 1·25), and in February, 1901 (distance 0·64), are clearly shown in the table.

It will be noted that in the final orbit the longitude of the descending node is $55^{\circ} 55' 8''$. The Earth will be in this longitude at the date, November 18, 1905, 10h., G.M.T. But from the final value of the mean anomaly it appears that the segment of the meteor stream to which these calculations refer, will pass through the descending node on October 16. In fact, from the final values of the elements which determine the form of the osculating ellipse, it appears that the orbit has become contracted in the 20 years' interval; the periodic time has altered from (the assumed) 6.667 to 6.612 years. Notwithstanding this contraction, on account of the large relative shift in the positions of the node and perihelion, the radius vector of the meteor stream when passing through the descending node at the next return will be 0.012 of the unit of distance, or about 1,100,000 miles, greater than that of the Earth when in that position in its orbit.

As the general result of these calculations, therefore, it appears that the most probable date for the centre of a shower of Bielid meteors this year is November 18, 10 h., G.M.T. If there be a shower at that date, it will indicate that the meteor stream is, in this part, of sufficient length to occupy at least 33 days (October 16 to November 18) in passing a definite point in its orbit—or that there is another swarm following the main swarm at this interval—and is also of sufficient extent in the direction Sun—Earth to allow of some of the meteors encountering the Earth, although the centre of the stream is more than 1,000,000 miles outside the Earth's orbit at the time.

These conclusions rest on the further (but very probable) assumption that the perturbations of the segment of the stream following the segment to which these calculations refer by 5° of mean anomaly are sensibly of the same amount as those given above.

I have to express my acknowledgments to Prof. A. S. Herschel, F.R.S., for his kind assistance in supplying information regarding the history of the subject, to Dr. P. V. Neugebauer for the care and skill with which he has computed the perturbations, and to the Council of the Royal Society for the allotment of a grant from the Government Grant, Urgency Fund to defray the necessary expenses.

On the Magnetic Qualities of some Alloys not Containing Iron.

By J. A. FLEMING, M.A., D.Sc., F.R.S. and R. A. HADFIELD, M.Inst.C.E.

(Received May 15,—Read June 8, 1905.)

The exhibition by one of us (Mr. R. A. Hadfield) at the British Association Meeting at Cambridge in 1904, of a sample of a magnetic alloy first prepared by Dr. Heusler, composed of copper, aluminium, and manganese, having aroused considerable interest, we felt that the quantitative measurement of the principal magnetic constants of such a material would be of very considerable interest. We, therefore, undertook at the earliest moment experiments with this object in view, and the following paper contains an account of the preliminary results obtained. For the purposes of exact magnetic measurements it was necessary to prepare the material in the form of homogeneous rings of regular form. This part of the work was undertaken at the Hadfield Steel Works, Sheffield, and in the early part of January, 1905, two such rings of alloys not containing iron were sent to the Pender Electric Laboratory of University College, London, for the magnetic tests.

These two rings were respectively numbered No. 1871 and No. 1888/7. Their chemical constitution was as follows:—The ring No. 1871 had the following composition: Manganese, 22·42 per cent.; copper, 60·49 per cent.; aluminium, 11·65 per cent. There is a certain amount of intermingled slag, probably 2 or 3 per cent., mostly consisting of MnO and SiO₂, and slight traces of other metals. Analysis showed that there was present also: Carbon, 1·5 per cent.; silicon, 0·37 per cent.; and iron, 0·21 per cent. Hence it may be said that nothing but a trace of iron occurs in this sample of alloy.

The other ring No. 1888/7 had an approximate composition: Manganese, 18 per cent.; copper, 68 per cent.; aluminium, 10 per cent.; lead, 4 per cent. These alloys unfortunately have poor mechanical properties and are brittle and cannot be forged. Rings were cast from the material and turned in the lathe to the desired form.

The rings having been carefully shaped, their dimensions were then measured. Both rings had approximately a mean diameter of 12·4 cms. and a square cross-section of approximately 1 cm. axial depth and 1 cm. radial breadth.

Each ring had four diametral lines, marked on it at angular intervals of 45°. As the ring No. 1871 was very slightly tapered, measurements were made on the front and back face and the means taken as follows:—

Outside Diameter of Ring No. 1871.

Along diameter.	At back in cms.	At front in cms.	Mean in cms.	Mean outside diameter = 12·3765 cm.
1—5	12·390	12·360	12·375	
2—6	12·384	12·358	12·371	
3—7	12·392	12·368	12·380	
4—8	12·390	12·370	12·380	

The axial depth and radial breadth were then measured in the same eight positions:—

Position.	Breadth.		Depth.	Position.	Breadth.		Depth.
	Back.	Front.			Back.	Front.	
1	1·056	1·050	1·060	5	1·060	1·042	1·056
2	1·056	1·044	1·052	6	1·064	1·046	1·058
3	1·058	1·044	1·058	7	1·062	1·046	1·058
4	1·058	1·050	1·062	8	1·064	1·042	1·054

The resulting mean dimensions of the ring are, as follows:—

Ring No. 1871.

Mean outside diameter	12·3765 cm.	Mean depth.....	1·0572 cm.
Mean inside "	10·2713 "	Area of cross-section	1·1129 square cm.
Mean breadth	1·0526 "	Length of magnetic circuit or mean perimeter	35·576 cm.

The ring was then carefully wound over with primary and secondary electric circuits. These consisted of double silk-covered copper wire, well insulated with shellac varnish.

The ring was first given a coat of shellac varnish made up with absolute alcohol and after drying was wound over with four separate secondary circuits, placed in the four quadrants. These each consisted of one layer of silk-covered copper wire (No. 30 S.W.G.) and were numbered respectively 1, 2, 3, and 4. The turns were counted by more than one observer and after varnishing and drying the outside width and depth over, the winding was again measured so as to calculate the excess of the area included by the median line of each secondary wire turn, over and above the cross-sectional area of the ring of alloy itself. The results were as follows:—

Secondary coil.	Number of turns of wire in coil.	Mean outside depth, in cms., over winding.	Mean outside breadth, in cms., over winding.
1	208	1.154	1.1415
2	197	1.152	1.137
3	204	1.150	1.140
4	207	1.150	1.135

The secondary coils were then covered with a layer of silk tape and varnished, and after drying, the primary magnetising coil was wound on in three layers. This consisted of No. 18 double cotton-covered copper wire, the three layers having respectively 217, 206, and 197 turns. Between each layer a winding of varnished silk tape was interposed.

The ring so wound over uniformly with secondary and primary coils was mounted on a board with screw terminals at the ends of the various circuits. From the dimensions taken, the mean area included by the central line of one turn of the secondary circuit can be calculated, and it is 1.2097 sq. cms. Since the mean cross-sectional area of the ring is 1.1129 sq. cms., the difference between these two must be reckoned as an air space which is traversed by the magnetic flux due to the primary coil alone.

The magnetic measurements were made in the usual way with a ballistic galvanometer. A Paul movable coil ballistic galvanometer, having a periodic time of about four seconds, was employed. The secondary coil on the ring was joined in series with the galvanometer coil, with a resistance box and with a secondary standardising coil, which last was inserted in the interior of a long helix or primary standardising coil, in which a known magnetic field could be created by a measured current. The currents were measured by a potentiometer. The usual methods were adopted for determining the magnetisation curve and the hysteresis loops of a sample of magnetic material in the form of a ring. A known primary current was reversed through the primary coil on the ring and the throw of the ballistic galvanometer observed.

The meaning of the deflection was interpreted by breaking or reversing a measured current through the primary standardising coil. It is not necessary to enter into details of the arrangements, as they are familiar to everyone in the habit of using the ballistic galvanometer for magnetic measurements.

The cyclical magnetisation curves were, in all cases, taken by applying to the ring a known maximum magnetising force, and then dropping suddenly from this to a smaller value in the same direction, or to one in the opposite direction. In this manner the change in the flux, passing through the secondary coil in passing from a certain maximum flux to a lesser or oppositely

directed flux, was determined and the cyclical magnetisation curves set out as usual.

Since the area included by the median line of one turn of the secondary circuit exceeds slightly the actual cross-sectional area of the ring, a necessary correction was applied in reducing the observations to obtain the true flux density in the metal itself from the observed or apparent flux density as calculated from the galvanometer deflections.

If B' is this observed flux density, B the true flux density, and H the magnetising force, then from the dimensions given above we have

$$1.1129 B = 1.2097 B' - 0.0968 H.$$

In the first set of observations an ordinary magnetisation curve was taken, with gradually increasing magnetising forces (H), the flux density (B) being measured by reversing the force at each stage, and the corresponding permeability values (μ) being calculated for each value of B . The reduced figures of observation are given in Table I.

Table I.—Magnetisation Curve of Magnetic Alloy No. 1871, taken with Magnetic Forces varying from 1 to 50 C.G.S. Units.

Magnetising force in C.G.S. units.	Magnetic flux density in C.G.S. units.	Permeability.	Magnetising force in C.G.S. units.	Magnetic flux density in C.G.S. units.	Permeability.
H.	B.	μ .	H.	B.	μ .
1.10	18.6	16.9	20.80	496.5	23.84
2.19	32.45	14.8	21.80	530.0	24.3
3.28	56.90	17.35	23.0	564	24.5
4.28	77.7	18.15	24.1	599	24.82
5.48	100.05	18.25	25.2	636	25.22
6.57	122.4	18.65	26.28	659	25.05
7.66	144.4	18.86	27.4	703	25.64
8.46	167.5	19.8	28.5	738	25.88
9.86	192.3	19.52	29.6	780	26.35
10.95	218.0	19.9	30.7	811	26.4
12.04	238.5	19.8	31.8	845	26.56
13.14	270.0	20.54	32.85	877	26.7
14.23	294.8	20.7	33.95	922	27.15
15.32	323.0	21.06	35.05	955	27.24
16.41	351.6	21.4	37.25	1030	27.66
17.50	385.0	22.0	39.45	1096	27.78
18.60	419.0	22.5	41.6	1162	27.94
19.70	464.0	23.32	43.9	1236	28.15

A second magnetisation curve was subsequently taken, carrying up to force to a much higher limit, viz., 225 C.G.S. units, as far as it was safe to go without destroying the insulation of the primary coil. The figures obtained are given in Table II.

Table II.—Magnetisation Curve of Magnetic Alloy No. 1871, taken with Magnetic Forces varying from 4 to 225 C.G.S. Units.

Magnetising force in C.G.S. units.	Magnetic flux density in C.G.S. units.	Permeability.	Magnetising force in C.G.S. units.	Magnetic flux density in C.G.S. units.	Permeability.
H.	B.	μ .	H.	B.	μ .
4·36	75·64	17·36	88·21	2163·1	26·00
8·74	160·21	18·34	88·20	2221·0	25·18
13·12	260·56	19·88	91·80	2272·7	24·76
17·45	344·33	19·78	95·98	2303·5	24·00
21·83	467·9	21·43	100·33	2385·0	23·77
26·23	597·96	22·80	104·92	2412·9	22·99
30·77	749·21	24·35	109·49	2441·3	22·30
35·26	844·36	23·95	113·71	2497·1	21·96
39·47	1054·0	26·70	118·26	2552·7	21·59
43·86	1207·1	27·53	122·93	2571·6	20·92
48·15	1358·1	28·20	127·0	2606·1	20·52
52·66	1463·9	27·79	131·68	2662·7	20·22
57·04	1604·9	28·13	136·0	2690·3	19·78
61·36	1714·3	27·94	140·09	2716·7	19·39
65·58	1828·1	27·87	144·79	2773·0	19·15
69·83	1911·0	27·37	149·42	2799·0	18·73
74·28	1966·9	26·75	163·5	2802·0	17·14
78·57	2049·5	26·09	225·43	3013·1	13·36

The observations recorded in Table II are plotted into a curve in fig. 1, and show that the magnetisation curve for this magnetic alloy possesses all the well-known characteristics of a magnetisation curve of the ferro-magnetic metals, iron, nickel, or cobalt. They show also that the permeability is a function of the flux density, and has a maximum value of nearly 28.

The next step was to take a number of cyclical magnetisation curves carrying the material through a magnetic cycle of operations, and employing various and increasing maximum values for the magnetic force.

In the Tables III to IX below, are recorded the reduced results showing the magnetic force and corresponding flux density in the case of the various cycles, the maximum value of the magnetic force in either positive or negative direction being given for each cycle.

The results of all these observations are embodied in a series of hysteresis loops or cyclical magnetisation curves, which are given in fig. 2. The range of maximum magnetic force for the various cycles extended from 10 to 70 C.G.S. units.

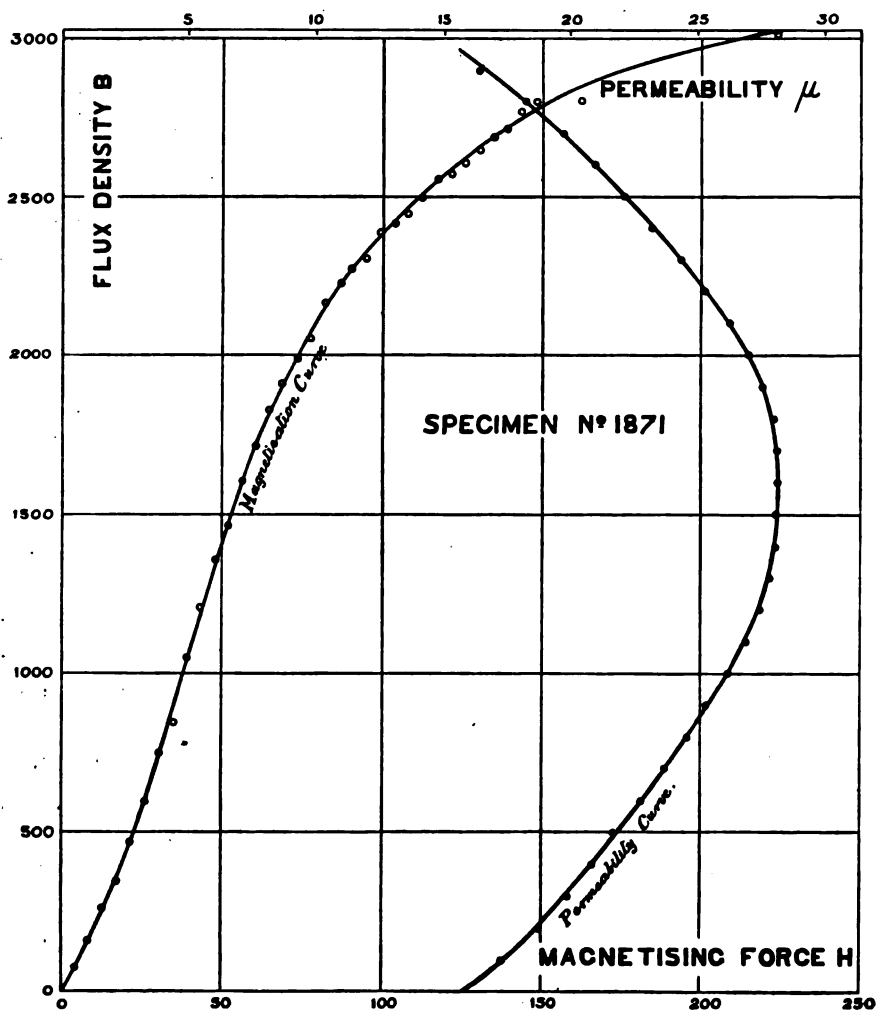


FIG. 1.—Magnetisation and Permeability Curves of Alloy No. 1871.

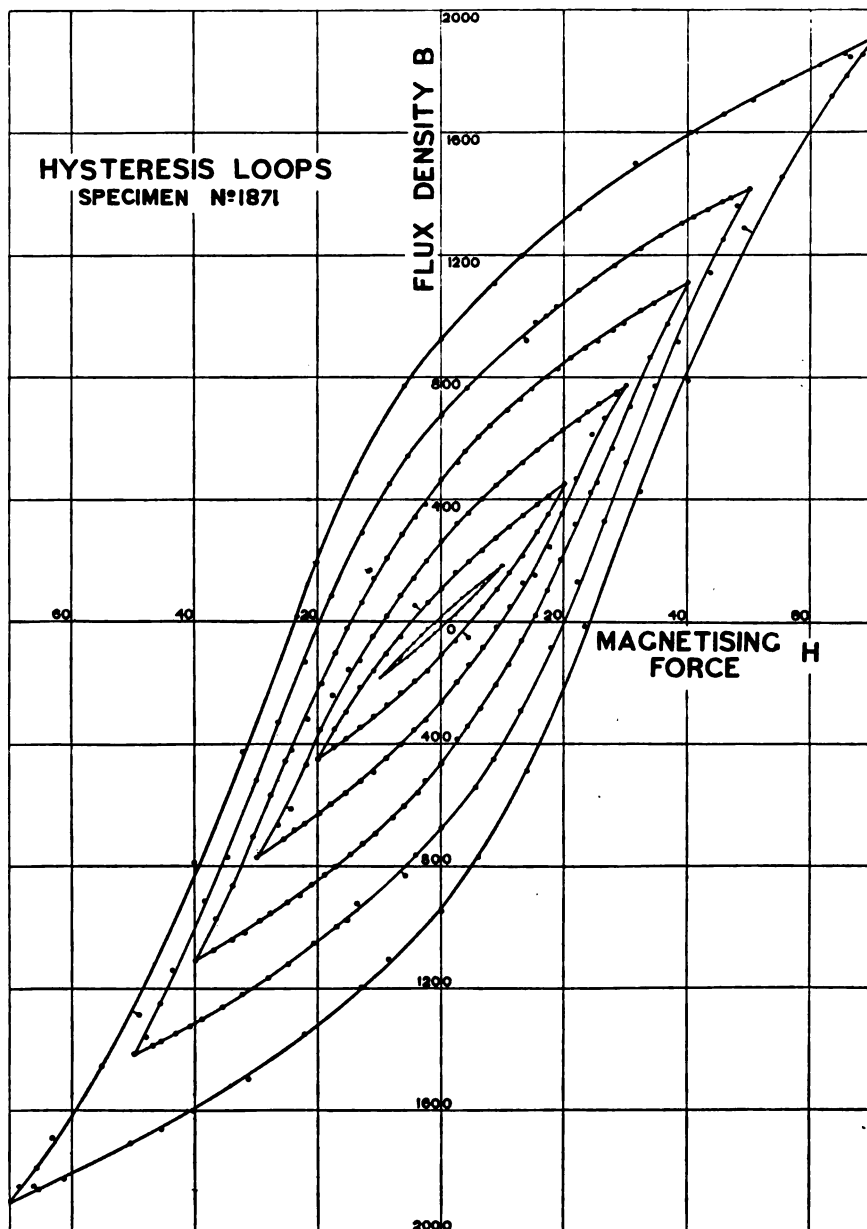


FIG. 2.—Hysteresis Loops of Alloy No. 1871.

Table III.—Cyclical Magnetisation Curve for Magnetic Alloy No. 1871.
Maximum Value of Magnetising Force = 10 C.G.S. Units.

Force positive and decreasing.		Force negative and increasing.	
Magnetising force in C.G.S. units.	Magnetic flux density in C.G.S. units.	Magnetising force in C.G.S. units.	Magnetic flux density in C.G.S. units.
+ H.	B.	- H.	B.
9·06	170·4	1·095	5·69
7·92	149·9	2·256	22·95
6·68	131·2	3·329	46·7
5·59	115·7	4·46	69·03
4·43	96·32	5·598	92·08
3·255	77·22	6·627	115·15
2·186	57·73	7·726	138·2
1·09	37·87	9·023	167·0
0·0	16·32	10·0	184·3

The numbers under the column headed +H are the gradually decreasing but positive values of H, to which the force is reduced each time from the maximum value +10.

The numbers under the heading -H are the negative values of H, to which the force is suddenly changed from +10.

The corresponding values of B delineate one-half of the hysteresis loop.

Table IV.—Maximum Value of Magnetising Force = 20 C.G.S. Units.

+ H.	B.	- H.	B.
17·42	413·4	2·31	61·85
15·496	385·0	4·44	6·00
13·17	347·6	6·69	49·85
10·96	310·6	8·90	105·7
8·796	275·2	10·95	161·5
6·633	233·8	13·16	217·4
4·44	195·5	15·48	295·6
2·295	162·2	17·45	351·6
0·0	106·5	20·0	452·1

Table V.—Maximum Value of Magnetising Force = 30 C.G.S. Units.

+ H.	B.	+ H.	B.	- H.	B.	- H.	B.
28·48	753·6	13·21	521·45	2·46	199·27	17·62	242·76
25·57	713·35	10·97	492·36	4·47	142·66	19·64	355·1
23·76	684·2	8·87	447·16	6·68	86·58	21·88	466·8
22·19	660·3	6·61	401·92	8·86	19·03	24·41	551·7
19·74	627·9	4·39	356·4	11·17	48·9	26·55	666·4
17·86	598·3	2·46	322·15	13·15	128·0	28·43	745·75
15·53	561·06	0·0	263·38	15·24	157·0	30·00	773·8

Table VI.—Maximum Magnetising Force = 40 C.G.S. Units.

+H.	B.	+H.	B.	—H.	B.	—H.	B.
37·01	1077·0	17·23	801·9	2·64	885·8	19·45	208·88
34·21	1042·7	14·69	762·7	4·29	343·1	21·65	319·98
32·32	1019·0	12·82	728·0	6·36	286·0	24·25	423·68
29·51	979·1	10·67	694·2	8·89	208·6	25·33	456·8
27·77	954·6	7·93	643·2	10·98	141·8	27·72	568·8
25·39	920·1	6·01	603·6	13·02	72·5	30·58	705·5
23·89	897·8	3·78	558·4	15·28	24·82	33·94	867·4
21·05	864·3	2·64	521·2	15·30	21·47	36·68	975·1
18·89	829·8	0	464·9	17·2	102·63	40·00	1112·0

Table VII.—Maximum Magnetising Force = 50 C.G.S. Units.

+H.	B.	+H.	B.	—H.	B.	—H.	B.
46·87	1888·8	24·91	1122·0	5·50	542·4	34·69	772·8
45·56	1876·1	22·33	1085·0	8·47	452·9	38·36	918·0
43·16	1850·8	20·73	1053·9	12·92	292·86	43·67	1144·0
40·88	1827·1	18·67	1031·8	17·77	87·69	45·66	1253·9
39·01	1803·8	17·04	999·4	22·15	132·1	48·0	1364·0
35·58	1264·6	15·26	975·5	26·52	331·1	50·0	1419·3
33·69	1245·7	13·69	922·1	30·08	522·0		
32·35	1221·9	5·91	830·9				
30·10	1189·3	4·25	768·8				
28·13	1167·3	0	674·8				

Table VIII.—Maximum Magnetising Force = 60 C.G.S. Units.

+H.	B.	+H.	B.	—H.	B.	—H.	B.
55·05	1561·5	27·56	1236·2	6·56	351·74	36·17	807·0
54·56	1559·1	22·25	1158·5	10·62	406·01	40·88	1003·0
50·05	1509·6	19·73	1122·0	15·16	240·29	45·53	1273·0
45·87	1460·4	14·2	1025·3	19·52	62·0	50·15	1449·8
40·58	1406·8	9·97	956·4	23·61	132·9	53·16	1557·3
36·10	1349·0	5·73	868·6	28·29	381·6	54·93	1613·1
32·35	1299·6	0	745·8	31·68	560·0	60·0	1612·9

Table IX.—Maximum Magnetising Force = 70 C.G.S. Units.

+H.	B.	+H.	B.	—H.	B.	—H.	B.
65·17	1859·9	31·60	1495·5	5·87	769·1	55·14	1457·8
61·42	1823·6	22·40	1350·6	13·88	487·2	63·33	1693·7
55·29	1763·2	13·51	1206·0	23·52	18·8	65·65	1797·5
50·52	1706·0	8·64	1115·8	32·14	429·4	66·35	1855·3
45·94	1664·0	0	925·6	40·12	790·2	68·65	1855·1
40·75	1604·1			49·14	1292·0	70·0	1904·9

The figures in the above tables having been set out in the form of hysteresis loops or cyclical magnetisation curves, the areas of these curves were taken in square centimetres, and by division by 4π , the energy loss in ergs per cubic centimetre per cycle of magnetisation was obtained. The final results are set out in Table X.

Table X.—Cyclical Magnetisation Curves and Hysteresis Energy Losses per Cycle of Magnetic Alloy No. 1871.

Maximum value of the magnetising force in C.G.S. units in each cycle.	Maximum value of the flux density in each cycle.	Energy loss in ergs per cub. cm. per cycle = area/ 4π .
$H_{\max.}$	$B_{\max.}$	E.
10	184.3	35.02
20	452.1	464.8
30	773.8	1589.2
40	1112.0	3600.4
50	1419.3	6336.0
60	1613.0	7258.0
70	1859.9	10880.0

From the figures in Table X a curve can be set out (see fig. 3) which delineates the relation between E and $B_{\max.}$, or the energy expenditure required to carry the magnetic alloy through one complete magnetic cycle of operations and the maximum value of the flux density during that cycle. This curve is shown in fig. 3 (on the left hand) as a curve concave upwards. If, instead of plotting in terms of E and $B_{\max.}$ as taken from Table X, we plot the logarithms of these quantities, we obtain a nearly straight line, as shown on the right-hand side of diagram 3.

The values in Table X show that the energy loss per cycle may be represented as an exponential function of the maximum flux density by an expression of the form

$$E = \eta B_{\max.}^n,$$

where n is some exponent and η some constant.

We find the numerical values to be best represented by the expression

$$E = 0.0005495 B_{\max.}^{2.238}.$$

The exponent n in the case of iron, nickel, and cobalt is a number not far from 1.6. In the case of this alloy the hysteretic exponent between $H_{\max.} = 10$ and $H_{\max.} = 70$ has a much higher value, viz., 2.238.

From the above observations we are then able to draw the following conclusions :—

(i) The alloy No. 1871, composed of copper, aluminium, and manganese, in the proportion mentioned above, exhibits magnetic properties which are identical with those of a feebly ferro-magnetic material.

(ii) The magnetisation (or B , H) curve is of the same general form as that of a ferro-magnetic metal such as cast iron, and indicates that with a

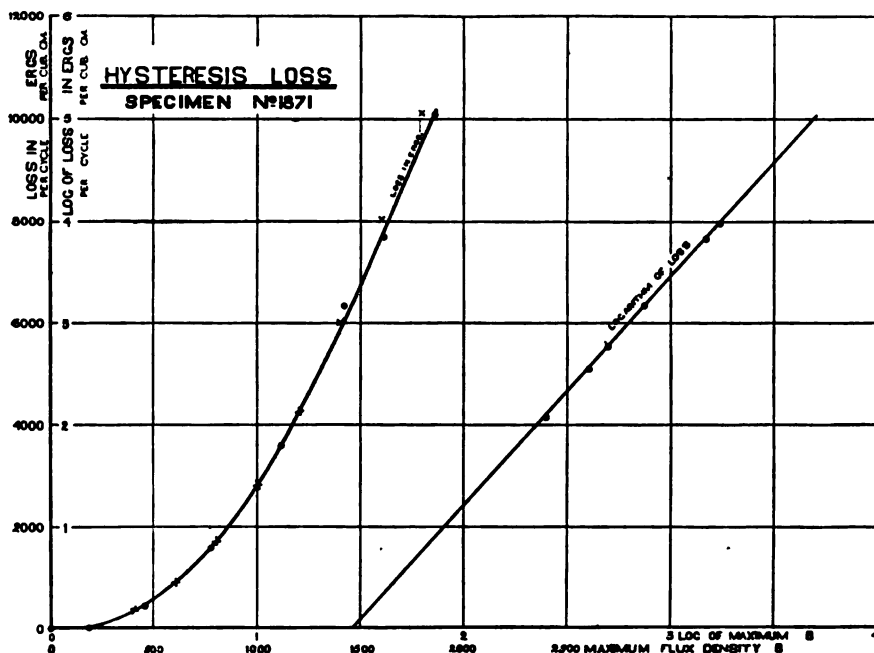


FIG. 3.

sufficient force, a state of magnetic saturation would most probably be attained.

(iii) The alloy exhibits the phenomenon of magnetic hysteresis. It requires work to reverse the magnetisation of the material and to carry it through a magnetic cycle.

(iv) The material has a maximum permeability of 28 to 30, which is not greatly inferior to that of the values reached for cobalt or a low grade of cast iron for small magnetic forces, and occupies a position intermediate between the permeability of the ferro-magnetic and the merely para-magnetic bodies, such as liquid oxygen and ferric chloride.

(v) The material exhibits, therefore, the phenomenon of magnetic

retentivity and coercivity. It is not merely magnetic, but can be permanently magnetised.

We are led by these results to conclude that the magnetic properties of this alloy must be based on a certain similarity of molecular structure with the familiar ferro-magnetic metals.

The hypothesis which best fits the facts of ferro-magnetism is that materials, such as iron, nickel, and cobalt, are composed of molecular groups which are permanently magnetic, and that the process of producing or changing the evident magnetisation of a mass of these metals consists in arranging or disturbing the positions of these molecular magnets. Since then, we have in this alloy an instance of fairly strong ferro-magnetism produced by an admixture of metals possessing in themselves separately no such property, it follows that ferro-magnetism *per se* is not a property of the chemical atom, but of certain molecular groupings.

The importance of this fact cannot be easily overstated. It shows us that in spite of the fact that ferro-magnetism has been hitherto regarded as the peculiar characteristic of certain chemical elements—iron, nickel, and cobalt—it may, in fact, depend essentially on molecular grouping composed of a comparatively large number of molecules, and, hence, it may be possible to construct alloys which are as magnetic or even more magnetic than iron itself.

[*Note added June 2.*—We have furthermore conducted experiments on the magnetic qualities of the alloy No. 1888/7, and we find them generally to be similar to those of the alloy No. 1871. The alloy No. 1888/7 has less manganese (about 5 per cent.) and more copper (about 8 per cent.) in it than the alloy No. 1871. In addition, alloy No. 1888/7 contains 4 per cent. of lead. The magnetisation curve of the alloy No. 1888/7 was taken with gradually increasing magnetising forces up to $H = 220$. The magnetisation curve is rather flatter than that of ring No. 1871, and the maximum permeability reaches a value of only 14 for sample No. 1888/7, instead of nearly 28. A series of hysteresis loops was taken between the same limits of magnetising force as in the case of ring No. 1871, and from their areas a curve set out showing the hysteresis loss in ergs per cubic centimetre per cycle (E) in terms of the maximum value of the flux density during the cycle (B_{\max}). We found that the relation of these two quantities could be expressed by an exponential function, viz. :—

$$E = 0.000776 B_{\max}^{2.238}.$$

Hence it appears that for both alloys No. 1871 and No. 1888/7 the hysteretic exponents are not very different, being respectively 2.238 and

2.288, whereas the hysteretic constants are very different, being respectively 0.0005495 and 0.000776.

It is clear, therefore, that both these alloys, although magnetic, have far greater hysteresis than pure iron, nickel, or cobalt, for corresponding cycles of magnetisation.

We hope to find opportunity of carrying out similar experiments at various temperatures, as the determination of the critical temperature at which these alloys will lose their magnetic susceptibility is evidently a very interesting matter.]

In conclusion, we desire to record our thanks to the actual observers who have taken the many thousands of observations necessary to obtain the figures here given. This observational work was done by Messrs. Westerdale, Bullman, Ramsay, Tarlton, and Nichols, students working in the Pender Electrical Laboratory of University College, London. The work was carefully superintended by Mr. W. C. Clinton, B.Sc., the demonstrator in the Pender Laboratory, to whom also thanks are due for the care with which it has been carried out.

*Preliminary Notes on Observations made with a Horizontal
Pendulum in the Antarctic Regions.*

By J. MILNE, F.R.S.

(Received May 29,—Read June 8, 1905.)

Amongst the various records brought home by the ss. "Discovery" from the Antarctic Regions, a long series refer to the movements of a horizontal pendulum. This instrument, which is similar to a type adopted by the British Association and established at 38 widely separated stations in various parts of the world, was in charge of Mr. Louis Bernacchi.

When we read Mr. Bernacchi's log we recognise the exceptional difficulties, meteorological and otherwise, under which he worked. This and the fact that a hurried departure only admitted of a few hours' instruction in the practical working of the instrument he had to use, entitle him to the sincerest congratulations on the results he has brought home.

From March 14 to November 9, 1902, the instrument with its boom pointing from north to south was installed in a hut with the magnetometers. It rested on a pillar made from an earthenware drain-pipe. From November 14, 1902, to December 31, 1903, it was placed on a brick column erected in a living hut. These huts were 30 to 50 feet above sea-level at a place in longitude $166^{\circ} 44' 43''$ E. and latitude $77^{\circ} 50' 50''$ S., about 15 miles distant from Mounts Erebus and Terror. The former of these volcanos was always active.

The records obtained refer to Changes in the Vertical, Tremors, Pulsations, and Earthquakes. In many instances these records when taken by themselves have little value, but when analysed in conjunction with registers obtained by similar and similarly installed apparatus at very distant stations they throw light upon hitherto unsuspected phenomena which take place within and on the surface of our world.

I. Changes in the Vertical.

Changes in the position of the outer end of the pendulum, which is an aluminium boom three feet in length, have been measured on the seismographic films at intervals of four hours, and in certain instances every 30 minutes. These films are strips of bromide paper each 2 inches in width and 35 feet in length. They moved beneath the end of the boom at a rate of 60 mm. per hour. The total length of film brought home by

Mr. Bernacchi is about 3000 feet. One millimetre deflection of the photographic trace of the outer end of the boom is approximately equivalent to a tilt of $0.5''$.

The measurement of the displacement of these traces was undertaken by my assistant, Mr. Shinobu Hirota, and Mr. Howard Burgess, of Newport, and it is in consequence of their kind assistance that the analyses of these records have reached their present stage. The results are at present in two forms—as a manuscript register and as a series of curves drawn on squared paper. Before the analysis of these records can be completed they must be supplemented with corresponding records from barographs and thermographs. The times of total darkness, continuous light, sunrise and sunset have already been entered on the squared paper. The times of sunshine and variations in atmospheric electrical conditions have not yet been obtained. Also, as Mr. Bernacchi remarks, tidal fluctuations, ice movements, changes in volcanic activity may also hold some relation to the wanderings of the pendulum. It is, therefore, desirable that information relating to these phenomena should be obtained.

A glance through the curves indicates that there have been many comparatively large and rapid deflections of the pendulum, particularly after its removal from the magnetic observatory to the living hut. For example, subsequent to the removal tiltings of $10''$ have taken place in 20 hours. Displacements of this magnitude suggest a yielding of the foundations or parts of the brick column on which the instrument was installed. My own experience is, that in England it takes about 12 months for a masonry pier to become stable. A pier made with a glazed earthenware drain-pipe has only its foundation to settle and becomes stable more quickly.

There are other deviations which may be seasonal, whilst others have accompanied marked barometric fluctuations. At certain periods there have also been changes in position of the boom indicating tilts of $0.5''$ to $1.0''$ which have approximately a diurnal periodicity.

In "Discovery" local time the western excursion of the pendulum was most frequently completed about 11 P.M., whilst it was usually farthest east about 3 P.M., and this took place whether there was sun or no sun. To explain these changes possible distortions produced by sun heat on the earth's surface have been invoked.

That an accumulation of a water load in a valley apparently causes its two sides to approach each other, whilst a body of men approaching an observatory will cause a pendulum inside the same to swing towards the advancing load, have strengthened the suggestions that changes of level observed at a station might be influenced by differences in evaporation or of vegetable transpiration

on opposite sides of such a building. These suggestions have each received careful attention.*

There is still another suggestion which I venture to make, and it is one which, for many reasons, I think, deserves consideration. Briefly, this is that the observed movements are not necessarily due to tilting, but are due to electrical attractions or repulsions. Factors to be taken into account when discussing this possibility are as follows:—

1. A small horizontal pendulum can apparently be made as sensitive as a gold-leaf electroscope, and, it may be added, might be used as an electrometer.

2. The Milne horizontal pendulum, by means of a quartz cup at the end of the boom and a silk thread at the top of the tie, is fairly well insulated, and responds to small attractive influences.

3. At Shide, the free south end of a boom which is pivoted at its north end at this season of the year (May) moves eastwards during the day and westwards during the night. A pendulum oriented east-west shows comparatively but little motion.

4. Movements take place when there is sunshine, even in a dark room, but with very cloudy or wet weather the movements are slight.

5. From an experiment now in progress at Shide an east-west pendulum since it has been connected to earth does not show the extensive movements it did prior to being earthed. With the co-operation of Dr. C. G. Knott, of Edinburgh, this experiment is being supplemented with others.

II. *Tremors and Pulsations.*

As shown in the films brought home by the "Discovery," tremors usually commence as intermittent slight thickenings. The thickenings recur at shorter and shorter intervals until there is a thickened line. This may have a width of 0.2 mm. The period of the movements they represent is probably near to that of the pendulum or 15 seconds. The duration of a storm usually lies between 6 and 20 hours. These thickenings may develop into serrations when we see that the period has been that of the pendulum. Regular movements with amplitudes of about 0.5 mm. and periods of 60 or 120 seconds are evidently forced vibrations, and are referred to as pulsations. These various movements have been tabulated as a register and also entered on squared paper with the curves showing changes in the vertical. They have not yet been analysed.

III. *Earthquakes.*

Between March 14, 1902, and December 31, 1903, although there were

* See 'British Association Reports,' 1895, pp. 115 to 139, and 1896, pp. 212 to 218.

many days when the instrument was not working, 136 earthquakes were recorded. As none of these were felt by the staff of the "Discovery," it may be assumed that none of them originated within 50 miles of the station on Ross Island. A certain number were recorded all over the world, whilst many were noted at very distant observatories. These latter must have originated at distances greater than 500 miles. The measurements of the various seismograms have been drawn up as a register, which, as far as possible, contains corresponding information from 43 other stations, 38 of which have seismographs similar to that used by the "Discovery."

The results of analyses which, however, are not yet completed, point to the following conclusions:—

1. *Distribution of Origins.*—Out of the 136 records, no less than 73 refer to disturbances which originated in a sub-oceanic region lying between New Zealand and the "Discovery." A certain number of these were only recorded by the "Discovery," and the exact location of their origin is very doubtful; others were recorded at Christchurch and Wellington, others again reached Perth, while some travelled as far as their antipodes.

On the maps published annually by the British Association to indicate the positions of origin of large earthquakes, 12 districts are shown. These are named by the letters of the alphabet from A to L. Districts J, I, L are not of great importance. The extremely active locality, the existence of which has been made known by the work of the "Discovery," I propose to call District M. The high frequency in the relief of seismic strain in the latter region indicates pronounced brady-seismical movement, an inference which is quite consistent with the existence of the active Erebus and many other recent volcanic peaks. It also suggests that New Zealand may be continued towards the south-west as a sub-oceanic ridge, accelerations in the growth of which are announced by sudden yieldings along its base. The islands of Auckland, Macquarie, and others may indicate the existence of such a ridge, but I am not aware that there are any soundings to confirm the suggestion.

Sixteen records refer to shocks which originated near Japan—the Philippines and the Celebes. Five had their centres in the Himalayan region, and six off the West Coast of South America.

Seasonal Frequency of Antarctic Earthquakes.

The relative frequency of disturbances with an antarctic origin in different seasons and months for the years 1902 and 1903 is shown in the following table. The numerals in the body of the table are the index numbers of earthquakes in the "Discovery" Register:—

	Jan.	Feb.	Mar.	Apr.	May.	June.
	Seismograph only working in 1903.	Seismograph not working.		9 10 12 15 16 18 20 21 77 78 79 80 82	28 31 32 34 { 67 68 84 85 { 86 87 89	33 35 36 40 41 90 92 95 97 98 99
No. of earthquakes	0	—	7	13	11	11
„ distinct seismic effects	0	—	4	12	9	11
	July.	Aug.	Sept.	Oct.	Nov.	Dec.
	43 100 103 105	108 110 113 114 115	{ 117 118 119	51 54 55 120 127 128 129	56 130 131 132 { 133 134	61 62 { 63 64
No. of earthquakes	4	5	3	7	6	4
„ distinct seismic effects	4	5	2	6	5	3

Earthquakes which are bracketed occurred within a few hours of each other, and, therefore, may possibly refer to the same relief of seismic strain. In the lower line of totals each of the groups has been regarded as a single disturbance. Whichever line we take, it seems that the greatest frequency has been in April, May, and June, or the first part of the winter months. The seasonal distribution of Antarctic earthquakes is, therefore, similar to the distribution noticed in many other countries. Dr. Omori, however, has shown that earthquakes with a sub-oceanic origin off the coast of Japan have their greatest frequency in the summer, during which season a higher average sea level more than counterbalances a diminution of load on the sea bed, due to a lower barometric pressure. This seasonal difference in load amounts to 18.3 mm. of mercury. Whether similar conditions prevail in the antarctic regions remains to be investigated.

On the Form of Areas Disturbed by Large Earthquakes.

For local earthquakes, such, for example, as are from time to time noted in Great Britain, we are prepared to see isoseists occasionally in the form

of circles, but more frequently in the form of ellipses. The major axis of any one of these ellipses is usually parallel to the strike of a fault, the sudden yielding on the face of which gave rise to the shaking. If the movement originates at no great depth, the epifocal area where motion is most pronounced has been shown by Dr. Charles Davidson to lie on the side of the fault towards which it hades.

With very large earthquakes, which are not sufficiently strong to be recorded over the whole surface of the world, but which may reach stations near to their antipodes, the idea of elliptical isoseists requires modification.

For example, earthquakes originating in District M to the south-west of New Zealand, have been recorded to the south-east by the "Discovery," and along a band about 20° in width, extending in a north-west direction as far as Britain. They may or may not be recorded in India, whilst at comparatively near places like Batavia, Manila, and Japan, lying northwards from the origin, they have been seldom noted. Also it may be added that they have not been noted at Cape Town, or at Cordova in Argentina, each about 80° distant, nor anywhere on the American Continents. It would appear, therefore, that recordable earthquake motion originating in District M may be propagated as a band running in a north-west direction as far as its antipodes. When more stations have been established in South America, it may be found that the motion proceeds to great distances in two directions round the world. This, however, is doubtful.

Earthquakes originating off the West Coast of South America have been recorded by the "Discovery" to the south-west, but the greatest length of recognisable wave-path is found towards the north-east in which direction they have been recorded in Western Europe and also near to their antipodes in Siberia. They have not been recorded at stations we should expect them to affect were they propagated with equal intensity in an opposite direction round the world.

Disturbances with origins in Japan, the Philippines, and the East Indies have been recorded as far south as the "Discovery" and westwards across Asia and Europe, whilst they do not appear to have reached nearer stations in North America. On the westward route it may be noticed that the path would be sub-continental, whilst in going eastwards it would be sub-oceanic.

The loudness of the sound made by a gun depends in part upon the direction in which the gun is trained with regard to the observer. In a somewhat similar manner, if we hold the blade of a spade in water and then suddenly move it, the largest waves are forced in the direction of the primary impulse.

If these analogies may be used to explain why earthquakes from District M are propagated more vigorously in a north-west direction rather than in any other, one inference is that the fault or faults from which these disturbances spring strike in a north-east and south-west direction, that is, they are parallel to the New Zealand axis, and they hade towards the direction of the longest path along which movement is recorded. Similar inferences may be made with regard to the origins of movements in other districts.

Velocity Determinations.—In a few instances, when accurate data have been obtainable, calculations have been made of the speeds with which earthquake motions have been transmitted in various directions round and through the world.

Speeds along paths which are continental are being compared with those which are sub-oceanic. For example, for earthquakes with origins off the coast of Eastern Asia, the rate at which waves have been transmitted across Asia and Europe may be compared with the rate at which the same travelled beneath the Pacific Ocean to New Zealand and the "Discovery." Certain tables relating to speed strengthen the suggestion that for particular phases of earthquake motion velocity is not constant. Other tables relating to rate of propagation are only of value as indications of the character of motion which has reached distant stations.

A knowledge of the time taken by earthquake waves to travel from one seismic region to another occasionally leads to the conclusion that one earthquake may be regarded as the final cause of a second disturbance. Illustrations of earthquakes having originated in a district at the times when teleseismic movement reached that district, are to be found in earthquakes numbered 4, 8, 45, 48, and 117.

The Surviving Phase of Earthquake Motion.

With exceptionally large earthquakes we may obtain at very distant stations seismograms which exhibit all three phases of earthquake motion. More frequently, however, at such stations the record is a mere thickening of the photographic trace, a small fraction of a millimetre in amplitude, and with a duration of 3 or 4 minutes. Near to its origin the maximum motion of the same earthquake may have been pronounced, while its total duration may have extended over at least 1 hour.

The test which has been used to determine the phase of motion to which the surviving tremors represented by a thickening are to be referred has been determinations of the speed with which they have been transmitted from their origin to the station at which they were observed. In a few instances the times of origin and the positions of epifocal districts have been obtained with

a fair amount of accuracy, and the results relating to earthquake speeds may be regarded as reliable determinations of the same.

This, however, is not the case with the majority of velocity tables which have been compiled, the reason being that they have been dependent upon data relating to times of origin and positions of centres which in all probability may in certain instances deviate by 5° in distance and 5 minutes in time from the truth.

Notwithstanding this, as the velocities of P_1 , P_2 , P_3 for long arcs are respectively about 12, 6, and 3 kilometres per second, although the velocities deduced for surviving phases may want in accuracy, they seem to be sufficient to suggest the type of wave to which they belong. The type determined appears to be P_3 , which at stations comparatively near to the origin is announced as an undulation of the earth's surface.*

On a Suspected Quadrantal Acceleration in Earthquake Speed.

The earthquakes here referred to are those which have been recorded at stations situated at distances of at least 90° from their origins. In well-defined seismograms these disturbances show three phases of motion. The preliminary tremors, or P_1 , reach stations 60° to 180° distant from origins with average chordal velocities increasing from 11 to 12 kilometres per second. These may be compressional waves. Following these a phase P_2 , which may refer to disturbance of body waves, which have over paths from 30° to 160° in length average arcual velocities increasing from 4.2 to 6.4 kilometres per second. Lastly, there is the maximum motion, or P_3 , which has an approximately constant arcual velocity of 3 kilometres per second.

For the commencement of this phase, which is apparently recorded as an undulating movement of the surface of the earth, and may therefore be regarded as being partially gravitational in character,† the velocity becomes 3.3 kilometres per second. With regard to P_3 , this, however, is a general statement. Within 10° of an origin, the value for P_3 appears to be less than 3 kilometres per second, whilst in the quadrantal region it may exceed 4 kilometres per second. These are also indicative of variation in velocity in the antipodean regions. The values for P_2 also appear to be increased in the quadrantal region. These velocity changes were first discussed in a British Association Report for 1900, p. 64 *et seq.*, but the data then at hand were not sufficient to sustain any definite conclusion.

The observations made by the "Discovery," taken in conjunction with observations referring to the same earthquakes made at other stations, have

* For list of shocks showing these survivals, see 'Antipodean Recurrences,' p. 292.

† The influence of gravitation has been discussed by Bromwich, in 'Proc. Lond. Math. Soc.'

added to the material illustrating the phenomena here considered, and it is for this reason that I have ventured to bring the subject to the notice of the Royal Society.

Something analogous to the movement recorded on the surface of the earth is seen in Whewell's Oceanic Cotidal Chart.* In the narrowest part of the Atlantic, between Africa and South America, the lines representing the hourly change in the position of the tidal crest are crowded together. As these travel northwards into the broader, and in places somewhat deeper, water, they are more widely separated. In other words, the tidal wave travels more quickly in the broader and deeper portions of ocean than in the narrower portions where it is retarded. Although the chart may not be "perfectly trustworthy,"† it at least suggests that a seismic wave of the type P_3 may be less constrained, and therefore travel more quickly in its quadrantal than in its polar region. This comparison is only intended to illustrate a form of progress, and not to suggest that the factors governing the variations in speed of the tidal and seismic waves are in any way identical. Further, the seismic wave at its antipodes shows an apparent increase in its velocity, which is the reverse of that which would be expected by a tidal wave when approaching the head of an oceanic inlet.

It might be assumed that the earthquake wave passes beneath a crust and over a nucleus, into which it merges. The upper portion of such a wave would be more retarded than its lower portion. It may also be imagined that the more swiftly moving lower portion on the first 90° of its path fails to give a surface indication of its existence because its external boundaries are widening. In the quadrantal region the periphery of the boundaries are fairly constant, and it is here that we find apparent acceleration in its speed. Still farther on its journey excessive contraction of the boundaries results in retardation of the waves.

This is merely a suggestion for the explanation of a phenomenon the true solution of which, as Dr. C. G. Knott points out, is in all probability to be found by a consideration of effects partially due to differences in the speed of surface waves and of body waves.

Antipodean Re-appearances.

For some years past I have noticed that earthquakes which had their origin in the vicinity of New Zealand, and were recorded in that country, have also been recorded in Britain, particularly at Bidstone, but had not necessarily been recorded at intermediate stations. The "Discovery" records

* See 'The Tides,' by G. H. Darwin, p. 172.

† *Ibid.*, p. 173.

taken in conjunction with those from Christchurch, Wellington, and Perth, have confirmed this observation, and we have now a number of instances where the movement from an epifocal area has travelled round and through the world, to re-appear as a recordable quantity at its antipodes.

It is not affirmed that in the region between an epicentral district and its pole seismic movement did not reach the surface of the earth, but only that even with instruments very much more sensitive than the Milne type motion has not been detected. The phenomena under consideration might also be described as antipodean resurgences, convergences, focal effects or *contrecoups*, each of which, however, might be objected to as implying an explanation for this antipolar relationship.

In the preceding registers we find the following 19 illustrations of possible re-appearances, viz.: Numbers 1, 32, 34, 51, 53, 59, 83, 89, 91, 93, 95, 96, 108, 111, 115, 117, 120, 129, and 130.

Out of these it seems that with earthquakes numbers 1, 34, 83, 89, 95, 96, 117, 120, and 129, the surviving phase has been P_2 . At Hamburg, Strassburg, and other stations where there are pendulums with a shorter period and a higher multiplication than those of the Milne type, P_1 has occasionally been recorded, *e.g.*, this is the case with numbers 1, 93, 111, and 130. In other instances the polar responses have been nearly simultaneous, a conclusion, however, which for many reasons may be more apparent than real.

The interpolar transit of a wave of the P_2 type may be compared with that of a deep-sea wave down a rapidly widening and then up a similar but rapidly narrowing estuary. The dimensions of these estuaries are assumed to be large. When half-way on its journey the height of the wave and its energy per unit area would be less than at its commencement or its terminus. It might, therefore, traverse the central area and not be noticed, but because of subsequent convergence it might become recognisable at points still further from its origin.

With very large earthquakes the movements were recorded all over the globe, and from experiments now in progress at Pribram, in Bohemia, the seismograms obtained at a depth of 1150 metres, although they show a diminished amplitude, they differ but little from those relating to the same disturbances recorded on the surface. The earthquakes we have to consider are of this type, but less in magnitude. Let us imagine one of these smaller efforts to start over an epifocal cap subtending 10° at the centre and that this expands as a ring 5° in width until it reaches the quadrantal region. The area of the cap or ring in the two positions will be approximately as 1 to 11, and if we neglect loss due to friction and assume constant energy, the intensity will be diminished in like ratio. With such conditions it seems

conceivable that a disturbance might be missed in the quadrantal region and recorded at its antipodes. The distance to which motion would invade the superficial region between the focus and the quadrantal region would depend upon the intensity of the disturbance at its origin.

The reappearance of P_1 , which is probably a condensational wave, may be accounted for by assuming that reflections are focussed in an antipodean region.

Dr. C. G. Knott, writing on this subject, says the phenomena may find its analogue in that which occurs in a whispering gallery. Imagine an earthquake starting at a good depth, somewhat deeper than the line which separates the fairly homogeneous nucleus from the heterogeneous crust. It is conceivable that under these circumstances the surface waves might not have time or opportunity to gather force. The disturbances might be mostly reflected at the higher incidences, that is, at the nearer parts of the hemispherical shell. After the quadrantal regions were passed, however, the waves would impinge at more acute angles, and the surface waves would be started in sufficient strength to make themselves appreciable. And note that, because of this very reflection at the nearer parts of the surface, there would be condensation towards the antipodal regions, there would be a greater supply of energy to draw upon in the production of the surface waves there. The theory is in fact that under certain conditions of start the surface waves would be started late, not exactly in the neighbourhood of the earthquake, but on towards the quadrantal regions.

Seismograms, Pulsations, Magnetograms, and the Value of g .

It is now well known that at certain observatories magnetic needles are frequently disturbed by unfelt earthquake motion. To throw light upon the consequent irregularities which from time to time are shown in the magnetograms at particular stations, horizontal pendulums have been established. The records given by the latter instruments are due to mechanical movements, but whether the corresponding perturbations shown in the magnetograms are due to a similar cause is by no means certain. At one station teleseismic movement may disturb surrounding and subjacent magnetic materials, with the result that needles at that station may respond to magnetic effects, which would not be the case at stations where the neighbouring materials which had been equally disturbed were non-magnetic.

At Ross Island the basalts are distinctly magnetic, while Mount Erebus and other recent cones indicate that physical and chemical characters, and also the arrangement of magnetic materials, have suffered change.

The varying activity of Erebus suggests that these hypogenic processes

have not yet ceased, and with seismic disturbances it seems probable that large bodies of magnetic magmas and rocks are at least temporarily disturbed and altered. We might, therefore, anticipate that the larger seismograms obtained by the "Discovery" would be accompanied by corresponding perturbations in the magnetograms. That a slight relationship of this description exists has already been noticed by Mr. Bernacchi, but now that the register of the "Discovery" has been extended this may be more clearly established.

When making this enquiry, large earthquakes which for various reasons were not recorded by the "Discovery" should not be overlooked. Also that the time at which disturbances of magnetic needles might be expected would probably correspond with the arrival of phase P_3 must be kept in mind.

To strengthen the assumption that "pulsations" are actual movements of the earth's surface, it would be of interest to compare the times when these were frequent with the periods when magnetic needles were unsteady or showed oscillatory movements.

The fact that the magnetic rocks on Ross Island have a high density is one reason which would lead us to expect a marked difference between the observed and calculated values for g .

*On the Application of Statistical Mechanics to the General
Dynamics of Matter and Ether.*

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The General Method of Statistical Mechanics.

1. One branch of abstract dynamics, which is, perhaps, best known under the name of Statistical Mechanics, attempts to discover as much as possible about the motion of a dynamical system when the specification of the system is either partially or fully known, but the initial configuration of the system is either not known at all, or is only partially known. A complete solution of the problem would require not only a full knowledge of the dynamical specification of the system, but also a full knowledge of the initial configuration of the system. These not being given, it is obvious that the problem cannot be fully solved.

The method of statistical mechanics is as follows: We divide up all possible configurations of the system into mutually exclusive classes, $A_1, A_2, A_3, \dots A_n$, and calculate the corresponding classes of solution after time t corresponding to the initial configurations of classes A_1, A_2, \dots . Let us call the final classes of solutions B_1, B_2, B_3, \dots . In selecting the original classes A_1, A_2, \dots , we arrange that the values of any co-ordinate in any class A shall differ so slightly from one another that the final values of the same co-ordinate in the solution B shall also only differ slightly from one another. The calculation proceeds by an appeal to the calculus of probabilities. Let $p_1, p_2, \dots p_n$ be the unknown probabilities that the co-ordinates of the initial system belong to the classes $A_1, A_2, \dots A_n$, so that

$$p_1 + p_2 + \dots p_n = 1.$$

Let us suppose that of the final classes $B_1, B_2, \dots B_m$, a certain number, $B_1, B_2, \dots B_m$, possess some special feature. Then the probability that the system shall possess this feature after time t is

$$p_1 + p_2 + \dots + p_m,$$

while the probability that it shall not possess this feature is

$$p_{m+1} + p_{m+2} + \dots + p_n.$$

Thus the odds in favour of the occurrence of this feature will be

$$\frac{p_1 + p_2 + \dots + p_m}{p_{m+1} + p_{m+2} + \dots p_n} \quad (1)$$

Let us suppose that a certain number, N , of the co-ordinates of the system all occur in exactly the same way in the dynamical specification of the system, so that the energy function is symmetrical in these co-ordinates. Then the value of the fraction (1) will be a function of N and of certain constants, c_1, c_2, \dots which enter in the specification of the system and in the probabilities p_1, p_2, \dots .

The procedure of statistical mechanics is to search for peculiarities for which the fraction (1) approximates to the limit infinity, when N is very great. Having found any such feature, we may say that it is infinitely probable that the peculiarity in question will present itself in the system after time t , this infinite probability being independent of the unknown law of probability of the initial co-ordinates. As regards practical applications to material systems, an infinite probability of this kind may be regarded as a certainty—*e.g.*, if the dynamical system is the universe, it is found to be infinitely probable that the entropy after time t will be greater than the initial entropy, a theorem which, for practical purposes, is stated with sufficient accuracy by saying that the entropy of the universe continually increases.

Application to a Holonomic Dynamical System.

2. In what follows it is assumed that the system under discussion is "holonomic"—*i.e.*, that its configuration at any instant is expressible in terms of a number of co-ordinates and their first differential coefficients with respect to the time, all these quantities being capable of independent variation. It is almost unthinkable that in dealing with the ultimate structure of the universe, as it is proposed to do in the present paper, we should be concerned with a non-holonomic system. Except in text-books, such systems can occur only through the massing together of a large number of independent co-ordinates into a smaller number, which nearly, but not quite, represent the larger true number. In fact, certain differences of independent co-ordinates are assumed to remain equal to zero absolutely throughout the motion, on the ground that, to make their difference vary perceptibly from zero, very great forces would be required. The actual independence of the obliterated co-ordinates shows itself, physically as a "force of friction," and mathematically as an equation of constraint of the kind which is not permissible in a holonomic system.

We assume, further, that the changes in the co-ordinates of the system are governed by equations of the canonical form

$$\dot{q}_r = \frac{\partial H}{\partial p_r} \quad \dot{p}_r = -\frac{\partial H}{\partial q_r}, \quad (2)$$

where H is the Hamiltonian function, and q_r, p_r are a pair of corresponding co-ordinates of position and momentum.

3. If these pairs of co-ordinates are N in number, we construct an imaginary space of $2N$ dimensions, any $2N$ orthogonal axes in this space corresponding to the values of the $2N$ independent co-ordinates

$$q_1, q_2, \dots, q_N, p_1, p_2, \dots, p_N.$$

Any configuration of the system can be represented by a point in this space, and if the point is to continue to represent the system, it must move in the space with the velocities determined by equations (2).

If we suppose the space filled with a continuous fluid, we can represent simultaneously the different motions of the system which correspond to all possible initial values of the co-ordinates. If, in the notation already used, we arrange the fluid so that initially masses a_1, a_2, \dots are found inside those parts of the space which represent the classes A_1, A_2, \dots , and if this fluid moves as directed by equations (2), then we shall find that after time t the regions of the space which represent classes B_1, B_2, \dots are occupied by masses a_1, a_2, \dots of fluid. The value of fraction (1), the probability that the system shall now possess the special feature considered, is

$$\frac{a_1 + a_2 + \dots + a_m}{a_{m+1} + \dots + a_n} \quad (3)$$

4. The first and most fundamental theorem of statistical mechanics expresses that the fluid moves as though incompressible. For, by the equation of continuity,

$$\frac{D\rho}{Dt} = -\rho \sum_1^n \left(\frac{\partial \dot{p}_r}{\partial p_r} + \frac{\partial \dot{q}_r}{\partial q_r} \right),$$

and this vanishes by equations (2), proving the theorem. Thus there is no tendency for the fluid to accumulate in any parts of the space, and the volumes which represent the classes B_1, B_2, \dots are equal to those of the corresponding classes A_1, A_2, \dots

5. If the full specification of the system were known—i.e., if the form of the function H , expressed as a function of the p 's and q 's, were known—it might be possible, by eliminating the time from equations (2), to obtain a number of integrals of the form

$$\begin{aligned} \psi_1(p_1, p_2, \dots, q_n) &= \text{constant}, \\ \psi_2(p_1, p_2, \dots, q_n) &= \text{constant, etc.} \end{aligned} \quad (4)$$

Equations (4) not only represent integrals of the equations of motion: they also represent families of surfaces in the $2N$ -dimensional space. These families of surfaces have the property that the particles of fluid in the space

can never cross them; the surfaces act as water-tight compartments between which the fluid moves.

6. If there are no integrals of the form of equations (4), every function of $p_1, p_2, \dots, q_1, q_2, \dots$ will in general vary with the time, and there will be no limits to the possible extent of this variation. Let χ be any function, such that those parts of the space in which χ is numerically less than a certain finite value χ_1 are finite in extent. There are plenty of such functions to be found—e.g., p_1, q_1 , the energy, etc. Then, if we select a point at random from the whole space, it is infinitely probable that the value of χ will be greater than χ_1 .

Suppose that we consider a system, or a point in the generalised space, starting from any initial value of χ , say χ_0 , and moving for an infinite time. Knowing nothing about the initial co-ordinates of the system, we may say that all points in the space are possible points for the representation of the ultimate state of the system. Moreover, since by the theorem of § 4 there is no tendency for the fluid to accumulate in any regions of the space, we may say further that all points in the space have equal chances of representing the final state of the system. Hence for a system starting from an arbitrary initial value χ_0 of χ , it is infinitely probable that, after a sufficiently long time, the value of χ will be greater than any arbitrary value χ_1 . In other words, the tendency of any function possessing the properties we have ascribed to χ is to increase indefinitely in value.

In the terminology of § 3, the special feature is that $\chi - \chi_1$ shall be positive; the fraction (3) becomes infinite through the number of terms in the denominator vanishing in comparison with the number in the numerator.

Irreversibility.

7. A tendency to increase such as that just found is generally described as an “irreversible phenomenon.” We see at once that these irreversible phenomena are inseparable from statistical mechanics. The irreversibility follows as a direct consequence of the absence of any tendency to aggregation on the part of the fluid in the generalised space, and this in turn is a consequence of the perfect reversibility of the original equations of motion.

In nature one function is known—namely, the entropy—which shows the tendency to increase indefinitely. Other of the possible χ -functions do not, so far as we know, show this tendency. The inference is that the hypothesis upon which we have been working, namely, that there are no water-tight compartments in the space, is not justified. There must therefore be at least one integral of the form of equations (4).

One integral, as we know, follows directly from the form of equations (2)

In particular, if the function H involves the momenta through terms of the second degree only, this integral is the energy integral, and it is consistent with our knowledge of the universe to suppose that the integral exists in this form.

We shall therefore suppose the generalised space divided into water-tight compartments by the family of surfaces

$$E = \text{constant},$$

while these compartments, again, may be subdivided to any extent by surfaces representing other integrals of the system.

Since E is necessarily positive, it is clear that E must be infinite at infinity in the generalised space, the loci $E = \text{constant}$ being closed or tubular surfaces, which, in general, decrease in size as the value of E decreases. The moving representative point no longer has access to the whole space, so that the argument of § 6 breaks down, and the function χ no longer shows a tendency to indefinite increase.

8. The phenomenon of irreversibility does not, however, disappear altogether. No matter how many integrals of the equations of motion there may be, it may still be true that in a single water-tight compartment some functions, χ, χ' , have the same value, χ_1, χ'_1 , at all except an infinitesimally small fraction of all the points inside the compartment, so that after the system has been in motion for an infinite time, it is infinitely probable that these functions will have the values χ_1, χ'_1 . Thus, the tendency of the functions χ, χ' , is always to move towards, never away from, the values χ_1, χ'_1 , and this tendency represents an irreversible phenomenon.

9. A good illustration is afforded by the Theory of Gases. In the development of this theory, it is found convenient at first to picture the molecules of the gas as rigid spheres, which together form a conservative dynamical system. The co-ordinates of position and momentum are the rectangular co-ordinates of the centres of the spheres and the components of momentum of the spheres respectively. The potential energy vanishes except during instants of collision, and these form only an infinitesimally small fraction of the whole time. The kinetic energy may accordingly be treated as constant, and this kinetic energy is equal, except for a constant multiplier, to the sum of the squares of the momenta. Let us examine the values of the momenta at each point of the space, and let us tabulate for each point of the space a function $f(q)$, such that the number of momenta at the point, of which the values lie within the narrow limits q and $q + dq$, form a fraction $f(q) dq$ of the whole. Then the function $\int_{-\infty}^{+\infty} f(q) \log f(q) dq$, which measures the value of $f(q)$ averaged for all the momenta at the point, is a

definite function of the co-ordinates of the point, and possesses the property that at all except an infinitesimal fraction of the points of any compartment, its value is *nil*. Thus, it is infinitely probable that in the final state of the gas the value of this function is *nil*, and as it can be shown that at all points at which the value of the function does not vanish, this value is necessarily positive, it follows that there is an irreversible tendency to a decrease of the value of the function. When the value of the function reaches its final zero value, the gas obeys Maxwell's law of distribution of velocities.

In a universe which consists of matter only, without ether, so that the energy is the sum of the energies of innumerable molecules, and of the potential energy of the intermolecular forces at work between the different molecules, it is easily shown that a similar irreversibility must be found, and that in the ultimate state of the system the energy is distributed in such a way that the average kinetic energy of each degree of freedom of each molecule is the same.

Statistical Mechanics of the Ether.

10. Let us next examine the statistical mechanics of a universe in which ether exists alone without matter. The energy in this universe consists of the energy of trains of waves in the ether. If the ether has any boundaries, these must not be regarded as capable of absorbing or storing energy, but as perfect reflectors impervious to energy. Trains of waves may differ as regards wave-length and direction, and after the wave-length and direction of a train of waves are known, the train will be specified dynamically by the values of one pair of co-ordinates. If we are considering a piece of ether limited by boundaries, we must replace the trains of waves by the principal vibrations of the ether within the boundaries.

In either case, the motion can be fully determined when the initial values of the co-ordinates are given, so that strictly speaking there is no need for the application of the methods of statistical mechanics. It will, however, be of interest to examine what information is obtainable by these methods. There is no interaction between the different trains of waves or principal vibrations, so that the energy of any train or principal vibration will remain constant. The equations which express the constancy of this energy are equations of compartments in the generalised space, and if $2N$ is the total number of co-ordinates, these equations are N in number. There are, however, other integrals to be obtained. The energy in either case is supposed to be of the form

$$2E = \sum_1^N (a_1 \dot{\phi}_1^2 + b_1 \phi_1^2),$$

so that ϕ_1 and $a_1\dot{\phi}_1$ may be taken as a pair of co-ordinates of position and momentum. The solution is known to be of the form

$$\phi_1 = A_1 \sin(p_1 t + \epsilon_1), \quad a_1 \dot{\phi}_1 = A_1 \sqrt{a_1 b_1} \cos(p_1 t + \epsilon_1),$$

where $p_1^2 = b_1/a_1$. Thus

$$\tan^{-1} \left(\frac{\phi_1 \sqrt{a_1 b_1}}{a_1 \dot{\phi}_1} \right) = p_1 t + \epsilon_1,$$

and we have the integrals

$$\sqrt{\frac{a_s}{b_s}} \tan^{-1} \left(\frac{\phi_s \sqrt{a_s b_s}}{a_s \dot{\phi}_s} \right) - \sqrt{\frac{a_1}{b_1}} \tan^{-1} \left(\frac{\phi_1 \sqrt{a_1 b_1}}{a_1 \dot{\phi}_1} \right) = \text{cons.} \quad \dots (s = 2, 3, \dots N),$$

$N-1$ in number. Thus the total number of integrals is $2N-1$, and the compartments are reduced to lines.

A certain number of functions of the co-ordinates can be found which do not remain constant throughout the whole length of a line, but which have the same values at all except an infinitesimal fraction of the whole space. As an example we have

$$\sum_1^N (a_1 \dot{\phi}_1^2 - b_1 \phi_1^2) = 0$$

at all except an infinitesimal fraction of the points. Thus, the method of statistical mechanics shows that the value of the function on the left hand tends to approach the value zero, i.e., the electric energy tends to become equal to the magnetic energy. This theorem, obvious enough from many points of view, is a theorem exactly analogous to the theorem of equipartition of energy in the theory of gases. It enables us to see very clearly the kind of irreversibility with which we are concerned in statistical mechanics.

Statistical Mechanics of Matter and Ether.

11. We shall next pass to the consideration of a system in which both ether and matter are present. At first we shall suppose the interaction between ether and matter to be very slight, although not actually zero. The advantage of this supposition is that the energy can be divided into energy of matter and energy of ether; just as, in the Theory of Gases, a similar supposition justifies us in dividing the energy into the sum of the energies of separate molecules.

The whole system can now be regarded as nearly equivalent to the aggregation of two systems, namely, the matter and the ether, and its co-ordinates will be very nearly the same as the aggregation of two sets of co-ordinates, namely, those of the ether, neglecting the presence of the matter, and those of the matter, neglecting its interaction with the ether. If ψ_1, ψ_2, \dots are

the functions of the co-ordinates of the material system which remain constant when the ether is left out of account, and χ_1, χ_2, \dots the similar functions of the co-ordinates of the ether, then the whole system of quantities

$$\psi_1, \psi_2, \dots, \chi_1, \chi_2, \dots$$

will nearly, but not quite, remain constant. No single one of these quantities can remain absolutely constant, for if it did, there would have to be either modes of vibration of the ether which could not be influenced by the presence of matter, a rather inconceivable supposition, or else it would be necessary that the values of the quantities which remain constant throughout the motion of the matter when the ether interaction is neglected should be uninfluenced by waves in the ether. These latter quantities, however, are known to be the energy and the six components of momentum of the material system, and the phenomenon of the pressure of radiation shows that all these quantities are altered in value by waves in the ether. The first possibility, however improbable, that there are ether vibrations which cannot be influenced by matter, need not trouble us. Even if there are such vibrations they are by hypothesis incapable of affecting the motion in any way, and they will be totally imperceptible to us, for our only perception of occurrences in the ether is derived through their influence on matter.

One quantity, we know, remains constant through the motion, namely, the total energy of ether and matter. This may be regarded as a modification of the equation which expressed, when matter alone was present, that the total material energy remained constant. The question arises as to whether there are other constants which may be regarded as modifications of the remaining constants of the separate systems. Although the material momentum parallel to the axis of x does not remain constant when the interaction with the ether is taken into account, yet it may be that there is some function of the ether co-ordinates which may be treated as ether momentum, so that the x -momentum of the ether plus that of matter may remain constant. All that can be said on this question is that if there are such functions, they are entirely unknown to us, and that it does not seem likely that the neglect of the constancy of any such quantities will invalidate the conclusions to be arrived at. We shall, therefore, proceed upon the assumption that the only constant is the energy.

12. It will simplify the problem to begin by considering either a finite universe, or else a finite portion of an infinite universe, enclosed within a perfectly reflecting boundary. Let the number of degrees of freedom of the matter inside this boundary, neglecting the interaction with the ether,

be N , so that there are $2N$ co-ordinates of the aggregate system which very nearly represent motion of matter only. The number N is known to be actually finite, although it may be supposed to be so large that the error involved in treating it as infinite will be negligible. Let the number of degrees of the ether be M , giving $2M$ co-ordinates to the aggregate system. If we suppose the ether to have an absolutely continuous structure, the number M will be absolutely infinite. If, on the other hand, we suppose the structure of the ether to be such that when magnified sufficiently it is found to be in some way coarse-grained—*e.g.*, if the ether were granular as imagined by Professor Osborne Reynolds—then the number M will be actually finite, although capable of being treated as infinite without perceptible error. In either case, M must be supposed large in comparison with N .

The energy of the $2M$ co-ordinates of the ether is, except for small terms arising from the interaction, expressible as a sum of $2M$ squares. The energy of the $2N$ material co-ordinates may, again neglecting small terms, be divided into kinetic and potential energy. The kinetic energy is expressible as a sum of squares, namely, the sum of the three components of energy of each electron of which the matter is composed. This statement requires modification if any perceptible fraction of the electrons move with velocities comparable with the velocity of light. We shall find it convenient at present to assume that the number of electrons moving with these high velocities is negligible. Also, if the electrons are sufficiently near to one another, the kinetic energy must be modified by the introduction of cross terms—products of two velocity components of different electrons—but the energy still remains quadratic in the components of velocity, so that it can be at once transformed to a sum of squares. Thus, the total energy is expressible as the sum of $2M+N$ squares, plus an unknown potential energy of electrons. It now follows, as in the proof of the well-known theorem of equipartition of energy, that throughout that compartment of the generalised space in which the system must now be represented, the sum of any p of these squares stands to the sum of the remaining q squares in a ratio which is equal to p/q at all except an infinitesimal fraction of the compartment, subject only to the condition that p and q are large enough to be treated as infinite without appreciable error. Since $2M$ and N satisfy these conditions, it follows that the system tends towards a state in which the energy of the ether is infinite in comparison with the kinetic energy of the matter. In other words, there is a general tendency for the ether to gain energy at the expense of matter.

It is, however, obvious that our own universe is at present far removed

from its final state, so that the study of this final state is of less interest than the study of the stages through which the final state is being reached.

13. In discussing the transition to the final state, a principle which I have proved elsewhere* will be of the greatest service. Suppose that a vibration of any dynamical system is influenced by an external agency. Then the principle in question asserts that the ultimate effect of this influence is infinitesimal, except when the external agency changes to a considerable extent in a time comparable with the period of the vibration. If the time of change in the external agency is n times the period of the vibration, where n is large, then the ultimate change in the energy of the vibration vanishes to the same order as e^{-n} , a quantity which soon becomes negligible as n increases.

Thus, if θ is some small interval of time, so small that the material system may be regarded as perceptibly unaltered through a time θ , then the change produced in the energy of ether vibrations of which the period is less than θ will be very slight. The energy of such vibrations may therefore be treated as though it were incapable of change, at any rate so long as our consideration of the system does not extend over a very long period. Hence certain of the ether vibrations, namely, those of shortest period, may be left out of account altogether, as has already been done in the case of the vibrations of the type discussed in § 11.

The total number of modes of vibration of any enclosed or unenclosed piece of ether is, as has been said, either very great or infinite, but the number of vibrations of an enclosed piece of ether of which the frequencies are below an assigned value is finite. Thus, we can now suppose M replaced by some smaller number M' , and the value of M' will be finite. So long as we limit our consideration of the system to a finite time, say a million years, we may regard the equations expressing the constancy of the energies of the remaining modes of vibration as water-tight compartments in the generalised space, so that the whole motion may be regarded as taking place in a generalised space of only $2(M' + N)$ dimensions. The ratio of ethereal to material kinetic energy which obtains through all but an infinitesimal fraction of this space is now $2M'/N$, a quantity which cannot be infinite and may be very small.†

It may be that there will be found to be other quantities besides the energies of ether vibrations of high frequency, which remain constant throughout enormous lengths of time. This possibility will be discussed later, but meanwhile a few considerations suggest themselves in connection with the results just obtained, and these it will be well to discuss now.

* "The Dynamical Theory of Gases," chap. 9.

† I have discussed the actual value of this ratio in another paper: "On the Partition of Energy between Matter and Ether," *Phil. Mag.*, July, 1905.

Radiation at a Given Temperature.

14. In the first place, it must be remarked that the conception of the "radiation corresponding to a given temperature" is not an exact conception. It depends on two quantities besides the temperature of the bodies inside the enclosure, namely, the shape and size of the enclosure and the time which has elapsed since the system was enclosed. For instance, it has been seen that after a system has been enclosed for an infinite time the radiation corresponding to any temperature is infinite, a result which is only reconciled with the finiteness of the total energy inside the enclosure by the temperature vanishing. To simplify as far as possible, the question of the dependence of the radiation on the time, let us suppose that at the instant at which the system is enclosed, the whole energy resides in the matter. If θ is a small time satisfying the conditions specified in § 13, then the rate at which an ether vibration of high frequency p gains energy will involve a factor $e^{-p\theta}$, so that the time required for the vibration to acquire a perceptible amount of energy will involve a factor $e^{p\theta}$. This is, of course, only true when $p\theta$ is large. At first, the energy of those vibrations for which $p\theta$ is not large increases, and a state will soon be reached in which these vibrations have the share of energy allotted to them by the theorem of equipartition of energy. With the progress of time the energy of the remaining vibrations gradually becomes perceptible, until ultimately the final state is reached.

15. We cannot, however, realise in nature the boundary impervious to all forms of energy, so that it is important to consider whether these predictions have to be modified if the boundary, instead of being perfect, is simply as perfect as we can make it. The imperfections of a natural boundary will be represented by supposing that the energy of the various ether vibrations leaks out through, or is absorbed by, the boundary at a certain rate. Let us suppose that the energy of ether vibrations of frequency p inside the boundary, is E per unit volume, and that the similar energy outside is E_0 per unit volume, then the best assumption to make is that the rate of leak is $k(E - E_0)$, where k is a constant. The rate of increase of E is now given by the equation

$$dE/dt = Ae^{-p\theta} - k(E - E_0),$$

where $Ae^{-p\theta}$ is the rate at which the energy E would increase if the boundary were perfect. The solution of the equation is

$$E = (E_0 + Ak^{-1}e^{-p\theta})(1 - e^{-kt}),$$

so that the ultimate value of E is $E_0 + Ak^{-1}e^{-p\theta}$. Experience shows that the value of E_0 must be supposed very small, while the value of the term $Ak^{-1}e^{-p\theta}$

has been supposed to be small on account of the exponential. Thus the energy of ether vibrations of high frequency tends towards a limit which is small in comparison with that predicted by the theorem of equipartition. The value of the total energy per unit volume of all the vibrations of high frequency, ΣE , tends to the value $\Sigma E_0 + \Sigma A k^{-1} e^{-p^2}$. Now, ΣE_0 , the energy per unit volume of these vibrations outside the boundary, is necessarily finite and is in point of fact known to be small. The number of modes of vibration of the ether inside any given enclosure, of which the frequencies are large, and lie between two near values of p , p and $p + dp$, is easily seen to be proportional to $p^2 dp$. Since the integral

$$\int_0^\infty e^{-p^2} p^2 dp$$

is convergent, it follows that the total energy of these high-frequency vibrations tends to a finite limit. Thus there is no longer any tendency for the energy of the matter to vanish in comparison with that of the ether inside the enclosure; the two tend to assume a finite ratio, although neither of the actual energies can be permanent, as the system inside the enclosure is no longer a conservative system. This definite ratio between matter and ether, however, lends a meaning to the expression "radiation at a given temperature," at any rate so long as we are concerned with the same enclosure and the same enclosed matter.

16. We may next discuss how this radiation at a given temperature will depend on the size of the enclosure. So long as the temperature and the nature of the matter remain the same, we may suppose that all vibrations of frequency below a certain value p receive their full share of the energy, while those of frequencies above p receive a fraction of their full share, the amount of this fraction depending only on the value of p . Now, as the linear dimensions of the enclosure vary, the number of vibrations of which the frequencies lie within any given range of values will vary as the cube of the linear dimensions, and therefore as the volume of the enclosure, provided the number in question is large.* Thus, the total energy of the ether will be proportional to the volume. If, then, we measure the intensity of radiation at a given temperature by the amount of ether energy per unit volume, we see that the intensity of radiation is independent of the size of the containing boundary. It is also easy to see that it will be independent of the shape of the vessel, although less easy to see how to construct a satisfactory formal proof of this statement.

In a sense, then, it is permissible to speak of the "temperature" of the ether inside the enclosure. If the system of matter consists of a number

* I have verified this for a rectangular boundary ('Phil. Mag.,' *loc. cit. ante*), and a similar proof is easily seen to hold for a spherical or cylindrical boundary. See also a letter by Lord Rayleigh, in 'Nature,' May 18, 1905.

of separate and disconnected bodies, we know that the radiation in the enclosure will tend to equalise the temperature of these bodies, and it is natural to think of the process as one analogous to conduction of heat, the ether in the final state possessing the same temperature as the bodies. We now see that this conception receives a large amount of justification from statistical mechanics. After agreeing, as a first approximation, to treat as invariable the energies of the rapid ether vibrations (and, if necessary, the rapid vibrations of the material systems), we find that the representative point in the generalised space appropriate to the representation of the problem, is constrained to move in a compartment in which the only variable co-ordinates are those corresponding to the slower modes of vibration of the ether, and certain of the co-ordinates of the material systems, these latter always including those which represent the motions of translation of the matter, *i.e.*, those which measure the temperatures of the different bodies in the enclosure. Throughout all except an infinitesimal fraction of the compartment, the mean energy of a material degree of freedom is equal to the mean energy of an ether degree of freedom, so that there is a tendency not only to the equalisation of the temperatures of the material bodies, but also of matter and ether. We say then that the ether has a temperature T , when this ether and a system of material bodies together in an enclosure have reached their final state, and this state is one in which the temperature of the matter is found to be T .

On the other hand, when we are told that hydrogen or oxygen is at a temperature T , we know the exact value of its kinetic energy per unit mass. This is not so with the ether; we know the energy of each of the graver vibrations, but we do not know how many vibrations have to be included in the total energy of the ether. For instance, in a mass of hydrogen at temperature T , the molecular movements are much quicker than those in a mass of mercury vapour at the same temperature, so that when an enclosure contains hydrogen, the number of vibrations which have to be considered in estimating the total energy of the ether is much greater than when the enclosure contains only mercury vapour. Thus the intensity of radiation depends not only on the temperature, but also on the nature of the matter with which it is in equilibrium.

Stefan's Law.

17. The next question which suggests itself is one of great importance. Given the nature of the matter, in what way will the radiation vary with the temperature? Stefan's empirical law states that the radiation is proportional to the fourth power of the absolute temperature, and Bartoli and Boltzmann

have attempted to raise the law to the level of a theoretical law, which can be predicted by thermodynamical considerations. The following is Larmor's form of statement of the argument.*

"We have to suppose an interior body A_1 at temperature T_1 , surrounded by an exterior body A_2 at temperature T_2 , but separated from it by a perfectly reflecting shell in the space between, which will prevent equalisation of temperature through passage of radiation from one body to the other. The spaces on the two sides of the shell will each be filled with radiation of the constitution and density corresponding to the temperature of the body on that side. We can imagine an ideal pump, constructed of perfectly reflecting material, that will pump radiation from the one side of this shell to the other, working against the difference of radiant pressure between the two sides: when the piston of such a pump is drawn out, the energy of the radiation that is isolated in the cylinder must be diminished by the work done by its pressure on the retreating piston. The result will be that if p_1 and p_2 are the pressures of radiation on the two sides, then for each unit volume of radiation transferred by the pump from outside to inside, the outer body A_2 must emit energy of amount $4p_2$, made up of the energy E_2 of the radiation and the work p_2 done by it on the piston, while the inner must absorb exactly what remains of this after the mechanical work W is performed. Now by Carnot's principle, we have for such an engine working reversibly between temperatures T_2 and T_1

$$\frac{H_2}{T_2} = \frac{H_1}{T_1} = \frac{W}{T_2 - T_1}.$$

In the present case, if the temperatures T_1 and T_2 on the two sides of the partition differ by a finite amount, the determination of the work W will involve an integration; let us, therefore, take the difference of temperatures to be infinitesimal, say δT , when the work will be equal to $p_2 - p_1$, or δp , to the first order. As H_2 is $4p_2$ or $\frac{4}{3}E_2$, we have thus

$$\frac{4}{3}E_2/T_2 = \frac{4}{3}\delta E/\delta T,$$

which yields on integration

$$\log E = 4 \log T + \text{const.}$$

Thus we arrive at the empirical law enunciated by Stefan, that the density of radiant energy corresponding to any given absolute temperature is proportional to the fourth power of that temperature."

18. The argument is seen to rest fundamentally upon the application of Carnot's principle to the working of the heat engine here described. The justification of Carnot's principle may be regarded as either empirical or

* "Ether and Matter," p. 137.

theoretical. As regards the empirical justification, it must be noticed that our experience is confined entirely to engines in which the working substance is material; there is not, and cannot be, any evidence as to the working of an engine in which ether is used as working substance. If it is argued that the principle is not known to fail in the case of any material substance, and that there is therefore a strong argument by analogy that the ether will not form a solitary exception, it may be replied that statistical mechanics explains quite definitely why the principle is applicable to all material substances, and proves with equal definiteness that it is not applicable to the ether. We come to this question in discussing the theoretical justification, or want of justification, for the principle when the working substance is ether.

Carnot's principle is, in effect, identical with the second law of thermodynamics, and this in turn is a special case of a special proposition in statistical mechanics. In the present investigation we have used the most general methods of statistical mechanics, and have arrived at a conclusion different from that of the second law. The general investigation ought, of course, to take precedence over the attempted extension of the special case. It is, moreover, easy to find the exact point at which the general argument parts company with that used in the special case. In the special case, we are dealing only with forms of material energy such that there is an easy and rapid transfer of energy to the final state. The increase of entropy, as has already been remarked, indicates simply the tendency to move towards this final state, and Carnot's principle is seen to be a special case of this general tendency in which it is supposed that the working substance is at every instant in the final state appropriate to its energy at that instant. When the ether is in question, we have seen that the transfer of energy, instead of being infinitely rapid, is, in point of fact, extremely slow, so that we never have to deal with a final state at all. The way in which the argument suitable to the special case of a material working substance breaks down when applied to the ether will, perhaps, be understood more clearly on considering an ether in which the special argument would be admissible. Such an ether is an imaginary granular ether, in which the transfer of energy from matter to ether is extremely rapid,* so that the radiation at any temperature is simply proportional to that temperature.

19. At the same time, the theoretical justification usually given for Carnot's principle is not one based on statistical mechanics, although it amounts ultimately to the same proof as that given by statistical mechanics, except that the theorem of equipartition is replaced by an appeal to experience in assuming

* Cf. "The Kinematics and Dynamics of a Granular Medium," § 20, 'Proc. Lond. Math. Soc.' (2), vol. 3, p. 124.

the tendency to equalisation of temperature. We can easily find in this more usual proof, the particular assumption at which the two cases of matter and ether as working substances must part company. It has to be assumed for the argument that the energy of the working substance is a function of only two independent variables, *e.g.*, the temperature and the density. This is not true in the case of an engine in which ether is the working substance; as we have seen, the ether energy is the sum of a number of vibrations of different wave-lengths, and the number of vibrations which have to be included in this sum will depend on the nature as well as on the temperature of the matter with which the ether is in communication.

Even if we avoid this objection, by considering only the cases in which all the matter is the same, we are left with a still more fundamental objection. Our analysis of the energy of the ether into a sum of energies of separate vibrations has rested on the supposition that the boundaries of the ether rested fixed. In the proposed argument for Stefan's law, the piston of the pump forms a moving boundary for the ether, such as has had to be specially prohibited. The action of such a pump would change the frequency of vibrations in the ether, and energy which at one instant belonged to a vibration of one period would, after passing through the pump, belong to a vibration of some entirely different frequency. The energy of the vibrations of high frequency no longer remains unaltered and very small, for there is a transfer of energy to these vibrations at every stroke of the pump. Thus the existence of the pump may be regarded as breaking down the water-tight compartments in the generalised space, and the only quantity which remains constant through a long interval of time is the total energy. The system will rapidly assume the final state appropriate to the value of this total energy, and this is a state in which the energy of matter vanishes in comparison with that of ether. Thus Bartoli's proof might be applicable to a universe in which pumps of the kind assumed had an actual existence, but has no application to our own universe in which the vibrations of highest frequency do not come into play at all. Moreover, if Bartoli's proof *were* applicable, the constant multiplying the factor T^4 would be infinite, so that we should have $T = 0$, except in a universe in which the energy per unit volume is infinite.

It will now be seen that in attempting to obtain a law of radiation in conformity with the analysis of the present paper, we shall not be able to use any method so general as that of the second law of thermodynamics. In fact, all general methods of this kind apply only to systems which may be assumed to be in their final states, while to determine the actual radiation we have to discuss the path towards this final state. The whole question is not one of partition of energy, but of transfer of energy.

Note Supplementary to a Paper "On the Radio-active Minerals."

By the Hon. R. J. STRUTT, F.R.S., Fellow of Trinity College, Cambridge.

(Received May 29,—Read June 8, 1905.)

In a paper read before the Society on February 28, 1905, I drew attention to the fact that all thorium minerals, so far as could be ascertained, appeared to contain uranium and radium. Since then, I have examined a number of additional minerals, in order to test the induction further. The result has been quite confirmatory of the original conclusion. I have, in this further investigation, contented myself with determining the thorium and radium, for it may now be considered proved that radium is a product of uranium, and it is much easier to establish the presence of radium by its emanation than to detect uranium by chemical analysis. The experimental methods explained in the former paper were employed. The results are as follows :—

Mineral.	Locality.	Thorium oxide, per cent.	Radium, millionths of 1 per cent.
Thorite	Ceylon	61·0	1·00
"	Brevig, Sweden.....	53·9	0·81
Monazite	Johannesberg	5·94	1·06
Alvite	Raade Moss, Norway	4·95	1·81
Xenotime	"	3·89	0·90
Monazite	N. Carolina*	3·79	0·53
"	Nigeria	2·98	3·78
Anerodite ?	Ceylon	2·27	9·80
Monazite	Malay Straits	1·53	4·02
Fergusonite	"	1·31	26·7
Malacone	Hitteroe, Norway.....	1·15	1·40
Allanite	Amherst Co., Virginia..	0·492	1·08
Yttrotantalite	Ytterby, Sweden	0·437	5·56
Polycrase	"	0·334	0·36
Zircon	N. Carolina	0·307	0·34
"	Virginia.....	0·217	0·52

In conclusion, I must express my best thanks to several friends, especially Professor W. R. Dunstan, for specimens of these minerals, which would, in some cases, have been impossible to procure otherwise.

* This consisted of pure grains of monazite, picked out from the commercial sand.

On the Intensity and Direction of the Force of Gravity in India.

By Lieut.-Colonel S. G. BURRARD, R.E., F.R.S.

(Received March 30,—Read April 13, 1905.)

(Abstract.)

Between 1865 and 1873, observations were taken at 31 stations in India by Captains Basevi and Heaviside with the Royal Society's seconds pendulums.

After 1874, when the pendulum work had been closed, the deflection of the plumb-line was systematically observed in all parts of the country. In 1901 a discussion of the evidence that had accumulated showed that determinations of the *intensity* of the force of gravity were badly wanted at many of the stations at which the *direction* of gravity had been measured, and in 1902 the Indian Government sanctioned the reopening of pendulum observations and the purchase of a new apparatus of von Sterneck's pattern.

Great weight was for many years attached to the Indian pendulum results of 1866 to 1873, but their accuracy has latterly been questioned.

In 1900, Professor Helmert laid before the International Geodetic Conference at Paris his celebrated classification of the pendulum observations of all countries, in which he discussed and weighed the results of all observers from the earliest to the most modern with an impartiality and a knowledge of details that have rendered his conclusions authoritative.

In this report, which is the only existing critical summary of pendulum work, it is pointed out that Basevi had no means of measuring the flexure of his pendulum stand, and that he had, moreover, during the original standardisation at Kew, supported his pendulums, not on the stand subsequently used in India, but between a stone pillar and a wall. Professor Helmert further shows that when Basevi visited the high Himálayan station of Moré, he substituted a light portable stand for that belonging to the Royal Society's apparatus.

The station of Moré—the highest pendulum station in Asia—was included in Basevi's programme at the request of Sir George Stokes; the extraordinary deficiency of gravity, observed there, formed the basis of Airy's and Pratt's theories of mountain compensation, and has been discussed by all authorities. In view of the wide extension of pendulum operations of recent years in Europe and America, and of the geodetic importance of Himálayan stations, it has been considered desirable to verify Basevi's results, and to increase largely the number of his stations.

In 1904, Major Lenox Conyngham observed with the new pendulum apparatus at four of Basevi's stations in India, and found that the latter's values were always too small.

Basevi's observations at Dehra Dun had lasted four months, and had included 234 independent sets of swings taken at widely varying pressures and temperatures; his first mean determination gave 86021·38 as the number of vibrations made by the mean pendulum in a mean solar day. His second determination gave 86020·74. Lenox Conyngham's recent observations show that these results are too small by *four whole vibrations*.

Lenox Conyngham's observations at Madras, Bombay, and Mussooree indicate, however, that Basevi's and Heaviside's results are not in error by a constant quantity. It seems probable that the flexure of the wooden stand of the Royal Society's apparatus varied with temperature and humidity.

Pendulum observations are required now at many stations in India to corroborate the results obtained from recent observations of the plumb-line. Prior to 1900, deflections of gravity were attributed to accidental and local attractions, but it has now been shown that they can be classified by regions. On all Himálayan meridians the direction of gravity has been found to follow one general law; in the neighbourhood of the tropic, as we move northwards, its direction changes from northerly to southerly; it continues then over the Ganges Valley to be deflected towards the south for some hundreds of miles, and it again becomes northerly as the Himálaya come into view. A marked southerly deflection of gravity has been found to prevail without interruption throughout the vast Indo-Gangetic plains of Northern India.

If an observer working over the plains of Northern India were to trust only to his eye and his level, he would record the existence of a great mountain range to the north, and of low hills or flat plains to the south; if, however, he were to disregard the evidence of eye and of level, and were to believe either his pendulum or plumb-line, he would come to the conclusion that he was standing between two mountain ranges, one of which, visible to the north, was rising abruptly out of the plains, whilst the other, invisible to the south, was slowly gaining in elevation for 300 miles. If he were to trust to his lines of spirit-levelling, he would find that Dehra Dun, at the foot of the Himálayas, was 500 feet higher than Kalianpur, in Central India; if he relied only on his pendulum results, he would discover Kalianpur to be 4700 feet higher than Dehra Dun.

The plumb-line at stations in Northern and Central India is thus influenced by two opposing attractions. A new determination of the resultant attrac-

tion at Kalianpur has now been made: at this station the attraction of the southern mass appears to be considerably greater than that of the northern and the resulting deflection of the plumb-line is calculated to be 6''·4 south.

Modified Apparatus for the Measurement of Colour, and its Application to the Determination of the Colour Sensations.

By Sir WILLIAM DE W. ABNEY, K.C.B., D.C.L., D.Sc., F.R.S.

(Received April 17,—Read May 18, 1905.)

(Abstract.)

The author describes a modification of his colour patch apparatus, in which two spectra are produced by the same beam that passes through the collimator and prisms. With this apparatus two distinct patches of pure or mixed colours can be placed side by side upon a white screen, and when a set of three slits is placed in each spectrum, mixtures in one spectrum can be matched with mixtures in the other, or with pure colours and white combined.

This new apparatus, in which also the positions of the slits in the two spectra could be most accurately determined, was used for a redetermination of the visual sensation curves.

The fourth sensation, supposed by Burch to exist in the violet, cannot be traced, and in the author's opinion is unnecessary. The amount of inherent white in the colour which best represents the green sensation is redetermined, and found to differ slightly from that found previously, as is also the amount of blue sensation in the yellow and green part of the spectrum. This last was only practicable by means of the new apparatus, which enabled pure colours to be isolated in one spectrum, and by mixtures matched in the other. There is also a redetermination of the three sensations in the other parts of the spectrum. The curves so determined vary slightly from those given in the author's previous communication.* In the full paper the various equations for the colour sensations are discussed, and examples in detail given, and finally the curves are tabulated, and the sensation curves for equal stimuli derived from them.

In another table the sensation composition in luminosities of the spectrum colours, when all white has been deducted, is given, and the plotted curves

* 'Phil. Trans.,' "The Colour Sensations in Terms of Luminosity," 1899.

of the three sensations and white show that there is no abrupt increase and consequent abrupt diminution in the white component. This is not the case in the curves which up to now have been given.

The sensation and "equal stimulus" curves are given for the normal spectrum. The latter part of the paper describes the use to which the last table can be put in ascertaining the dominant wave-length of any mixed colour, and the amount of white mixed with it. By the use of the table the luminosity of the colour can be found, as also its composition in terms of the three sensations. Examples are given, and the application that can be made of the results in making colour sensitometers for colour photography.

*On the Thermo-electric Junction as a Means of Determining the
Lowest Temperatures.*

By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S.

(Received May 16,—Read June 8, 1905.)

The inconvenience of using the gas thermometer at very low temperatures and the failure of platinum and other metal-resistance thermometers within 30° or 40° of the absolute zero, led me some years ago to consider the experimental behaviour of the thermo-electric junction at the lowest temperatures. My special object at the time the experiments were made was to have a further confirmation of the melting point of hydrogen, and also of the lowest temperature reached on exhausting solid hydrogen, other than that I had found by means of the hydrogen gas thermometer.* The results have remained unpublished, because my intention has always been to extend them to other thermo-electric combinations. Not having been able to accomplish this project, they are now abstracted as affording useful information in this field of investigation, and as furnishing a general confirmation of my previous investigations.

A German-silver platinum couple was selected as likely to give the most uniform results at low temperatures, although subsequent experiments have led to the conclusion that it would have been better to have replaced the platinum by gold. As regards resistance thermometers, I have shown that gold is more reliable than platinum at temperatures near the boiling point of

* "The Boiling Point of Liquid Hydrogen, determined by Hydrogen and Helium Gas Thermometers," 'Roy. Soc. Proc.,' vol. 68, 1901.

hydrogen.* The difficulties of the investigation were considerable: it had to be carried out at the time in the neighbourhood of the machinery producing the liquefied gases required in the investigation, namely, oxygen, nitrogen, and hydrogen, so that the zero of the delicate galvanometer employed did not remain quite constant. To remedy this I inserted a rocking make-and-break in order to get the readings of each observation at both ends of the scale. In the process of removing one difficulty another presented itself, through the development of small but appreciable thermo-electric currents in the rocker. Precautions had to be taken against these and at all other metal junctions against similar small thermo-electric currents, and it was even found necessary to have a correction on account of the resistance box, inserted in the circuit to bring large readings within the limits of the scale. The galvanometer and resistance box were inserted in the German-silver branch of the couple, the points of junction of the copper leads with the German-silver ends of the couple being insulated and placed close together within a vacuum test-tube packed with cotton wool to ensure equality of temperature.

Preliminary experiments showed that the junctions altered after having been subjected to the temperature of liquid hydrogen. However, on re-soldering the junctions with hard silver solder instead of soft solder, the thermo-couple accurately repeated observations at the temperature of liquid oxygen, after having passed through a liquid hydrogen bath. From this it appears that all such couples before calibration ought to be cooled suddenly in liquid air and then rapidly heated to the ordinary temperature, a similar operation being repeated with liquid hydrogen. If the couples return to their original state after such abrupt changes of temperature, then they are in a fit state for calibration.

Three series of observations were made to determine whether the resistance of the junctions varied to a noticeable extent with the temperature, namely, at the freezing point of water, at the boiling point of oxygen, and at the boiling point of hydrogen. Six very concurrent observations with varying resistances in the resistance box were made between 0° C. and 15° C. These were reduced by the method of least squares, and gave for the resistance of the circuit 3·500 ohms. Five similar results between the melting point of nitrogen and the boiling point of oxygen gave, by least squares, 3·293 ohms. Only two observations were taken in liquid hydrogen, which are therefore not entitled to the same weight as those already given, but the resistance appeared again about 3·3 ohms. As the variation of the resistance of the circuit was so slight, an attempt was made to reduce the results on the

* Bakerian Lecture, "The Nadir of Temperature and Allied Problems," 'Roy. Soc. Proc.,' vol. 68, 1901.

assumption of constancy, but this was not satisfactory. However, on treating the variation of the resistance of the circuit as linear with the temperature, the data came into better agreement.

The following table contains the details of the observations made with the silver soldered German-silver platinum couple, the recorded readings of the galvanometer being the means of several observed readings, corrected when necessary for resistance introduced into the circuit:—

No. of expt.	Substances used for difference of temperature.	Corresponding absolute temperatures.	Mean absolute temperature.	Mean galvanometer reading.	dE/dt .
1	Water at 15° and ice	280°, 278°	280½°	463.2	30.88
2	Boiling carbonic acid and ethylene	185, 170	182½	693.5	27.74
3	Boiling ethylene at 10 mm. and oxygen	123½, 90½	107	724.0	21.94
4	Boiling oxygen and nitrogen ...	90½, 77½	84	279.0	21.46
5	Boiling nitrogen and melting nitrogen	77½, 62½	70	330.7	21.88
6	Boiling hydrogen and melting nitrogen	62½, 20½	41½	623.5	14.84
7	Boiling hydrogen and melting hydrogen	20½, ?	?	51.0	?
8	Boiling hydrogen—solid hydrogen about 20 mm.	20½, ?	?	64.0	?

where dE/dt is the quotient of the mean galvanometer reading by the difference of the temperatures in the third column.

On plotting the first six of these results the 1st, 2nd, and 6th and means of the other three, viz., $dE/dt = 21.59$ at $t = 87^\circ$, lie nearly on a continuous curve (fig. 1). The continuity of the curve, without any approach to abrupt

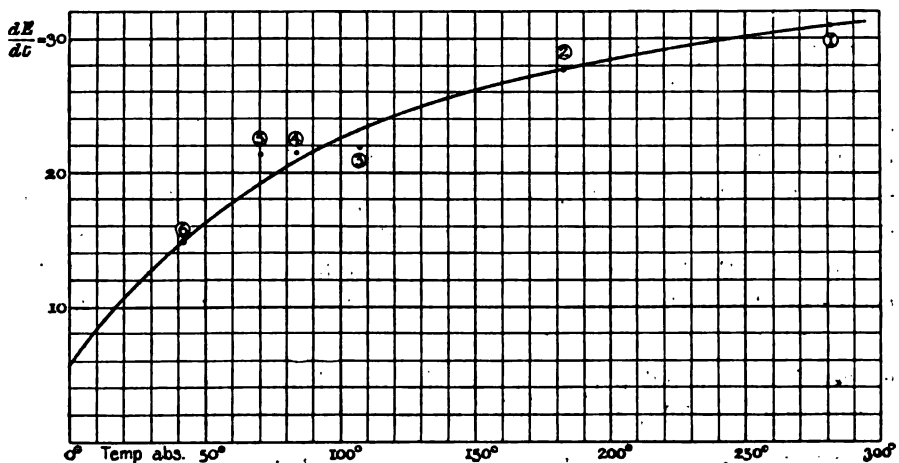


FIG. 1.—Thermo-electric Junction.

change of form, even in the region of liquid hydrogen, shows that a silver-soldered German-silver platinum couple is an efficient instrument for the determination of the lowest temperatures hitherto reached. For example, we may employ the curve (fig. 1) to determine the temperature of the hydrogen under exhaustion in observation No. 8. A graphical examination of the curve in the neighbourhood of the boiling point of hydrogen shows that we may write

$$dE/dt = 10.2 + \frac{1}{6}(t-18), \quad \text{or} \quad dE/dt = 7.2 + \frac{1}{6}t,$$

as an equation holding true for a few degrees above or below 18° absolute. Hence if x be the required temperature, we have

$$\frac{64}{20\frac{1}{2}-x} = 7.2 + \frac{20\frac{1}{2}+x}{12} \quad \text{or} \quad 20x^2 + 1728x = 28469,$$

one of whose roots is 14.15 . From the graphical analysis of the curve therefore we find the temperature of the hydrogen under exhaustion in the last observation to be $14^\circ.15$ absolute, or some $6^\circ.3$ below the boiling point. Similarly for observation No. 7 the temperature is found to be $15^\circ.50$.

From the results a curve with electromotive force, E , as ordinate, to absolute temperature, t , as abscissa, may be drawn, and this may be taken as a parabola, with the equation

$$(t+a)^2 = p(E+b). \quad (1)$$

For another point t' , E' , we have

$$(t'+a)^2 = p(E'+b),$$

whence, subtracting,

$$E' - E = p^{-1}(t' - t)(t' + t + 2a). \quad (2)$$

Any pair of observations will give p and a , after which, assuming any given point, for example H_{BP} , as origin, and putting $t = 20\frac{1}{2}^\circ$ absolute and T for $t' - 20\frac{1}{2}$, we get the equation connecting difference of electromotive force and difference of temperature

$$E' - E = p^{-1}T\{T + 2(t+a)\}.$$

An average value of dE/dt from (2) is equal to $\frac{E' - E}{t' - t}$, that is

$$= p^{-1}(t' + t + 2a);$$

but the correct value of dE/dt at a given point is, from (1),

$$\frac{dE}{dt} = \frac{2}{p}(t+a).$$

Now the fact that the Tait-line does not remain straight, but bends downwards as we approach the absolute zero, indicates that the parabola is being distorted as we approach its vertex, just as if the vertex were being

pushed up. To look for a straight line near the vertex therefore we must keep to observations near the vertex. I have therefore taken the four sets, Nos. 3, 4, 5, 6, from the table, similarly marked on the diagram (fig. 2), in which the highest extends from ethylene exhausted, $123\frac{1}{2}^{\circ}$ absolute, to the B.P. of oxygen, $90\frac{1}{2}^{\circ}$ absolute.

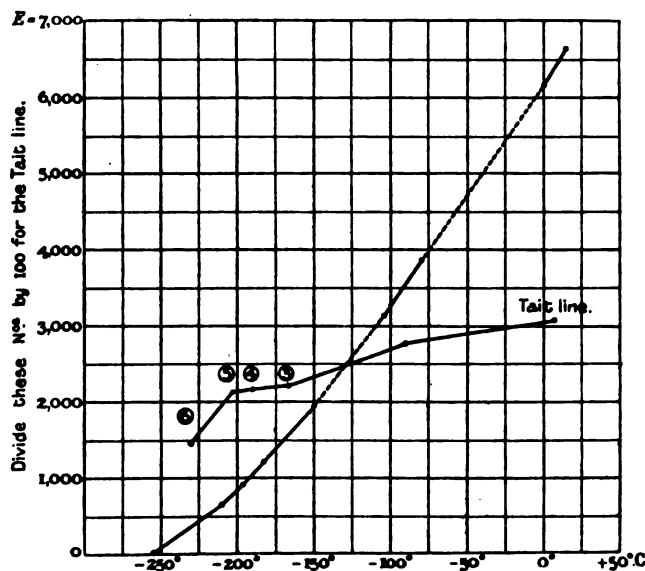


FIG. 2.—Thermo-electric Junction.

These corrected observations are:—

Range.	Temp. abs.	$E' - E.$	$t' - t.$	$t' + t.$
(3) Ethylene exh. to boiling oxygen	$123^{\circ} \cdot 5$ to $90^{\circ} \cdot 5$	724·0	33	214
(4) Boiling oxygen to boiling nitrogen	$90 \cdot 5$ „ $77 \cdot 5$	279·0	13	168
(5) Boiling nitrogen to melting nitrogen	$77 \cdot 5$ „ $62 \cdot 5$	320·7	15	140
(6) Melting nitrogen to boiling hydrogen	$62 \cdot 5$ „ $20 \cdot 5$	623·5	42	83

Hence equations of form (2), re-arranged more conveniently for calculation, are—

$$\begin{aligned}
 (3) \quad & 33 \times 214 + 2a \cdot 33 = p724 \quad \text{or} \quad 214 + 2a = 21 \cdot 9p. \\
 (4) \quad & 13 \times 168 + 2a \cdot 13 = p279 \quad \text{„} \quad 168 + 2a = 21 \cdot 5p. \\
 (5) \quad & 15 \times 140 + 2a \cdot 15 = p320 \cdot 7 \quad \text{„} \quad 140 + 2a = 21 \cdot 4p. \\
 (6) \quad & 42 \times 83 + 2a \cdot 42 = p623 \cdot 5 \quad \text{„} \quad 83 + 2a = 14 \cdot 8p.
 \end{aligned}$$

Taking (3) and (6), we get $p = 18.45$, and $2a = 190.0$. Therefore $E = \frac{1}{18.45} T(T + 231)$, reckoning from H_{BP} as origin. Hence for $E = -51$, we have

$$(T + 115.5)^2 = 115.5^2 - 51 \times 18.45 = 111.4^2.$$

Therefore $T = -4.1$, or H_{MP} is $4^{\circ}.1$ below H_{BP} , or is $16^{\circ}.4$ absolute.

For $E = -64$, $T = -5.23$, or $H_{exh.}$ is $5^{\circ}.23$ below H_{BP} , or is $15^{\circ}.27$ absolute.

From (3) and (6), reckoning from H_{BP} as origin, we get

$$dE/dt = 12.52 + 0.108T.$$

There is hardly a doubt that dE/dt at H_{BP} is not so great as 12.52, so that, as was anticipated, the $E_{th.exh.} - O_{BP}$ observations are too far away from H_{BP} to give a workable formula.

Taking (4) and (6) we get $p = 12.69$ and $2a = 104.8$.

Therefore $E = \frac{1}{12.69} T(T + 145.8)$, reckoning from H_{BP} as origin. Hence for $E = -51$ we have

$$(T + 72.9)^2 = 72.9^2 - 51 \times 12.69 = 68.3^2.$$

Therefore $T = -4.6$, or H_{MP} is $4^{\circ}.6$ below H_{BP} , or is $15^{\circ}.9$ absolute.

For $E = -64$, $T = -5.8$, or $H_{exh.}$ is $5^{\circ}.8$ below H_{BP} , or is $14^{\circ}.7$ absolute.

From (4) and (6), reckoning from H_{BP} as origin, we get

$$dE/dt = 11.49 + 0.158T.$$

In like manner from (5) and (6) we get $p = 8.64$ and $2a = 44.8$, whence $E = \frac{1}{8.64} T(T + 85.8)$, reckoning from H_{BP} as origin.

For $E = -51$, we get $(T + 42.9)^2 = 42.9^2 - 51 \times 8.64 = 37.4^2$, and therefore $T = -5.5$, giving the melting point of hydrogen $5^{\circ}.5$ below its boiling point, or $15^{\circ}.0$ absolute; and when $E = -64$, $T = -7.0$, or the temperature of the hydrogen under exhaustion was $13^{\circ}.5$ absolute. Observations (5) and (6) also lead to the equation

$$dE/dt = 9.931 + 0.231T,$$

with the boiling point of hydrogen as origin of temperature.

It is of importance to examine how an alteration of any of the constants in the formulæ employed affects the temperature deduced.

Choosing any assigned temperature as origin, the value of dE/dt at T° from that origin is given by an equation of the form $dE/dt = m + nT$.

But if the value assigned to dE/dt is obtained by dividing the difference of electromotive force D through the range of temperature T by T , then

this value of dE/dt must be assigned to the mean temperature $\frac{1}{2}T$, and the formula becomes

$$D/T = m + \frac{1}{2}nT, \text{ or } D = mT + \frac{1}{2}nT^2,$$

a quadratic for the determination of T , when D is known.

When the constant n alone varies, differentiating we have

$$dT = -\frac{1}{2} \frac{T^2}{m + nT} dn.$$

Thus if $m = 9.931$, $n = 0.231$, and $T = -7^\circ$, we get

$$dT = -\frac{49}{16.628} dn = -2.947 dn;$$

hence for $dn = -0.031$, $dT = +0.101$, showing that an alteration of n from 0.231 to 0.200 would only alter T from $-7^\circ.0$ to $-6^\circ.9$; or, roughly, a 10-per-cent. change in n at this temperature would only affect the temperature by 1 per cent.

When the constant m alone varies, differentiating we have

$$dT = -\frac{T}{m + nT} dm;$$

hence, in the same circumstances as before,

$$dT = -\frac{-7}{8.314} dm = 0.842 dm;$$

and thus, for a change $dm = 0.119$, the corresponding change of temperature is $dT = 0.100$, or if m were altered from 9.931 to 10.050, T would again be changed only from $-7^\circ.0$ to $-6^\circ.9$.

We may in a similar manner consider the effect of an error in the reading D on the deduced temperature.

$$\text{For } dD = (m + nT) dT, \text{ or } dT = \frac{1}{m + nT} dD,$$

giving, in the case already considered, $dT = 0.12 dD$, so that an error of a unit on D would only alter the value of T by an eighth of a degree.

These numerical results may be summarised by saying that, in the neighbourhood of the temperature of solid hydrogen under exhaustion, it would require an alteration of $1\frac{1}{2}$ per cent. in the values of D or m , and as much as 13 per cent. in the value of n , to alter the value of T by one-tenth of a degree.

In general, it may be noted that for an alteration of the same actual (but small) magnitude in the values of n , m , and D respectively, the corresponding alterations of T are proportional to $\frac{1}{2}T^2$, T , and 1.

The general results with the German-silver platinum junction may

be summarised in the following table, the typical equation being $dE/dt = m + nT$.

Source of constants.	<i>m.</i>	<i>n.</i>	Melting point of hydrogen.	Solid hydrogen exhausted.
(3) and (6)	12·52	0·108	16·4	15·27
(4) „ (6)	11·49	0·158	15·9	14·7
(5) „ (6)	9·931	0·231	15·0	13·5
Graphically	10·2	0·167	15·5	14·15
Mean	—	—	15·7	14·4

For reasons already mentioned, the temperatures deduced from the (5) and (6) set of experiments are in all probability the most accurate in the thermo-electric series of observations.

It is interesting to compare these results with those given in my former paper on the “Boiling Point of Liquid Hydrogen determined by Hydrogen and Helium Gas Thermometers.”* Although the main object of that paper was the accurate determination of the boiling point of hydrogen, I included in the experiments the recorded temperature of solid hydrogen under exhaustion of from 30 to 40 mm., as given by a hydrogen gas thermometer filled initially at a pressure of 269·8 mm. at 0° C. This thermometer gave the boiling point of hydrogen as 19°·63, and the solid under exhaustion as 14°·34; in other words, the gas thermometer value is just about a mean of the results given by the thermo-junction. This is, so far, confirmatory of the reliability of the thermo-junction as a thermometric agent at the lowest steady temperature we can command.

Although it is not recorded in the paper on the “Boiling Point of Hydrogen,” I found that the same helium thermometer which I used for determining the boiling point gave in exhausted solid hydrogen the temperature of 13°·65, but as the helium had to be corrected for the presence of a small amount of neon, the result might be a little too low. My intention at the time was to defer the consideration of the temperature of solid hydrogen for a further communication to the Royal Society, as distinctly stated in the original paper.

It is true that in a paper on “Solid Hydrogen,” read at the British

* ‘Roy. Soc. Proc.’ vol. 68, 1901.

Association in 1899,* that is two years before, I gave the approximate melting point of hydrogen as between 16° and 17° absolute. This value was based on observing the melting-point pressure of solid hydrogen as being about 55 mm., and therefrom calculating what the temperature should be at this pressure by means of a mean Rankine formula. From the later experiments contained in my paper of 1901 a more accurate Rankine formula can be deduced, viz., $\log p_H = 6.2874 - 68.02/t$, and this gives the approximate temperature of $14^{\circ}.96$ as corresponding to 55 mm., thus bringing the melting point given by the gas thermometer into substantial agreement with the lowest thermoelectric value.

As a record of the behaviour of the German-silver platinum thermojunction the following table has been calculated from the equations derived from the set of observations (5) and (6), namely:—

$$E = \frac{1}{8.64} T(T + 85.8) \quad \text{and} \quad \frac{dE}{dT} = 9.931 + 0.231T,$$

when one of the junctions of the couple is assumed to be kept in boiling hydrogen, and the other either falls or rises through a range of some 15° on either side of this temperature, which is about $20\frac{1}{2}^{\circ}$ absolute. These values show that, at as low a temperature as 6° absolute, the sensibility of this couple is still half what it was at $20\frac{1}{2}^{\circ}$ absolute, and therefore that, unless some absolute breakdown in the law connecting electromotive force and temperature below 14° takes place, it must continue to be an excellent thermometer, and will record temperature with considerable accuracy down to the boiling point of helium, which is about 5° or 6° absolute. A further paper will detail the results obtained in the study of the behaviour of helium at low temperatures.

<i>t</i> abs.	dE/dt .	E.
•		
35	13.281	168.32
32	12.588	129.51
29	11.895	92.77
26	11.202	58.09
23	10.509	25.55
$20\frac{1}{2}$	9.931	nil
18	9.354	– 24.10
15	8.661	– 51.12
12	7.968	– 76.05
9	7.275	– 98.90
6	6.582	– 119.70

* 'Nature,' September 21, 1899.

I am indebted to Mr. J. D. H. Dickson, M.A., of St. Peter's College, Cambridge, for help in the discussion of the results, and to Mr. Robert Lennox, F.C.S., for assistance in the conduct of the experiments.

Studies with the Liquid Hydrogen and Air Calorimeters.

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.

I.—*Specific Heats.*

(Received May 25,—Read June 8, 1905.)

The calorimeter employed in the following experiments was similar to that described in my paper on "The Scientific Uses of Liquid Air,"* and in an improved form in Madame Curie's work "Recherches sur les Substances Radio-Actives," 2nd edition, p. 100. A sketch of the apparatus appears in my paper on "The Absorption and Thermal Evolution of Gases Occluded in Charcoal at Low Temperatures."†

The arrangement employed consists essentially of a large vacuum vessel capable of holding 2 or 3 litres, into which is inserted a smaller vacuum vessel of 25 to 50 c.c. capacity constituting the calorimeter, the latter being sealed on to a long narrow tube which projects from the mouth of the exterior vessel, in which it is lightly held by a loose packing of cotton wool. A little below the upper end a branch tube is taken off which conveys the volatilised gas from the calorimeter to the gas receiver. To the extremity of the projecting tube a small test-tube, to hold the portions of substance experimented on, is attached by a short piece of rather wide rubber tubing which forms naturally a movable joint that can be bent into any position. With care I have found this valve gives as good results as more elaborate means of securing the dropping of the substances into the calorimeter. A small vacuum vessel which may contain either solid carbonic acid, liquid ethylene, or liquid air, into which the test-tube is placed, cools the materials to different temperatures below those of the laboratory; or alternatively the substances may be heated in the vapour of water or other liquids.

* 'Roy. Inst. Proc.,' 1894, vol. 14, p. 398.

† 'Roy. Soc. Proc.,' 1904, vol. 74, p. 123.

The general constants for liquid gas calorimeters are given in the following table :—

Liquid gases.	Boiling point.	Liquid volume 1 gramme at boiling point in c.c.	Latent heat in gramme calories.	Volume of gas at 0° and 760 mm. per gramme calorie in cubic centimetres.
Sulphurous acid	+ 10° 0	0.7	97.0	3.6
Carbonic acid	— 78° 0	0.65 (solid)	142.4	3.6
Ethylene	— 108° 0	1.7	119.0	7.0
Oxygen	— 183° 5	0.9	53.0	13.2
Nitrogen	— 195° 6	1.3	50.0	15.9
Hydrogen	— 252° 5	14.3	125.0	88.9

Thus an instrument in which liquid air is used has twice the sensibility of a corresponding one in which liquid ethylene is employed, whereas the substitution of liquid hydrogen for liquid air increases the delicacy of the calorimeter some seven times. It is easy to detect the transference of $1/50$ of a gramme calorie in the liquid air instrument, whilst $1/300$ of a gramme calorie can be similarly observed in the liquid hydrogen form of the calorimeter.

In preparing for use a liquid air calorimeter, some 2 litres of old liquid air containing a high percentage of oxygen are poured into the large silvered vacuum vessel, and the calorimeter, filled with some of the same fluid, is immersed therein. An experiment is conducted by tilting up the little test-tube previously cooled or heated, thereby dropping into the calorimeter a portion of any substance previously weighed. The substance, if left under normal conditions, in this way falls from the temperature of the room to that of liquid air. The heat given up by it to the liquid air volatilises some of it, which is carried off by the branch tube and measured in a graduated receiver. Immediately preceding or following this observation, a similar experiment is made with a small portion of a selected standard substance, namely, lead. The quantity of lead is so chosen as to produce about the same volume of gas in the receiver as that supplied by the portion of substance experimented on. By this means, the circumstances of the two observations are made as similar as possible, and thereby many sources of error are eliminated.

The handling of the instrument has been carefully studied and improved since the earlier experiments. I find that the vacuum of the calorimeter itself should be a mercury vacuum. Before inserting the calorimeter into the vessel of liquid air, it should have a good deposit of mercury over its surface, obtained by placing a little liquid air in the interior of the calorimeter and allowing it to stand for some time. After a considerable

quantity of the liquid air in the calorimeter has been volatilised, the boiling point of the remaining portion rises slightly above that of the exterior mass of liquid air, and the liquid over which the volatilised gas is collected is apt to "suck back." When this takes place the calorimeter should be emptied and filled anew from the external vessel. The tube coming from the calorimeter ought to be of the size of wide quill tubing, and the free end of the branch tube should be so arranged below the surface of the liquid in the collecting vessel as to produce no resultant pressure. With these precautions it is easy to get results accurate to within 2 per cent.

The use of pure oxygen has no advantage over that of liquid air which has stood for some days, and thus contains a high percentage of oxygen. Pure nitrogen cannot be used without taking special precautions to prevent the atmosphere from getting access to the calorimeter, as otherwise the air liquefies and causes great uncertainty in the working of the instrument.

When liquid hydrogen is similarly used, precautions have to be taken to keep air from getting condensed to the solid state in the neck of the calorimeter. For this purpose, a slow current of dry hydrogen, from an ordinary Kipp apparatus, is kept discharging, partly through the aperture by means of which the bodies fall into the calorimeter, and partly through the tube by which the evaporated hydrogen escapes to the receiver, until everything is ready to make the experiment. The hydrogen is led in by means of a T-shaped piece of tubing, with a stop-cock attached, placed between the calorimeter and the gas-collecting receiver.

When the body has to be transferred from solid carbonic acid or liquid air to the calorimeter, the following procedure is adopted:—It is placed in the small test tube, above the indiarubber joint, which is inserted into a small vacuum vessel containing some of the substance (solid carbonic acid or liquid air), so that at the moment of making the experiment the solid, by a quick vertical movement of the vacuum vessel, is thrown into the calorimeter. A little cotton wool inserted in the mouth of the vacuum vessel prevents the carbonic acid paste, or liquid air, from being ejected.

Among the sources of error which may occur, the following should be noticed and allowed for. In dropping a small body from the temperature of the laboratory (say) into liquid air, the range of temperature through which the body passes in $1/3$ or $1/4$ of a second is some 200° . Some of its heat will be lost to the vapour of the gas in the tube before it reaches the liquefied gas; and some at its various impacts on the walls of the glass-tubing, as it passes on to the calorimeter. The consequence of these losses will be to make the quantity of gas measured in the collecting receiver err by defect. Experiments were made with cooled substances to estimate the effect of a

similar error in the opposite direction. It was found that 1 gramme of lead, ejected at the temperature of liquid air into the calorimeter filled with liquid air, absorbed enough heat on its passage to produce 1 c.c. of air in the gas receiver; roughly, 1 gramme of lead falling through 200° into liquid air produced 100 c.c. of air in the receiver; hence, in this case, the error is within $1/2$ per cent. A similar observation with diamond gave 1.8 c.c. in comparison with 150 c.c.—an error of about $6/10$ per cent.; and graphite gave some 4 c.c. in comparison with 300 c.c.—an error of about $2/3$ per cent. Such errors may be neglected in these results.

The observations were reduced by comparison with lead. The method of comparison has obvious advantages. Each day when experiments were being made on any substance, a concomitant series was made on lead, so that unknown errors would affect the results equally, and thus produce volumes of gas in the receiver accurately proportional to the quantities of heat carried into the calorimeter. The choice of the particular metal in question was based on the following considerations:—The low specific heat of lead enabled small quantities of heat to be conveyed into the calorimeter while the mass of metal was still considerable; the variations in the specific heat of lead with temperature are small, and are very nearly a linear function of the temperature; and lastly this metal is easily obtained very pure.

The values taken for the specific heat of lead were:—

Between $-252^{\circ}\cdot5$ and -188° , or at $-220^{\circ}\cdot5$,	specific heat = $0\cdot0280$
„ $-188^{\circ}\cdot0$ „ -78° „ $-133^{\circ}\cdot0$ „	= $0\cdot0290$
„ $-188^{\circ}\cdot0$ „ $+18^{\circ}$ „ $-85^{\circ}\cdot0$ „	= $0\cdot0295$

From calculations based on these values, an error of a degree in the first of these ranges would only affect the specific heat by $0\cdot000006$; a similar error in the second range would produce the same variation in the specific heat; and in the third range the variation would be $0\cdot000004$. Hence a variation of from 10° to 20° in any of these ranges would not affect the given values of the specific heat noticeably.

As a selection the following may be taken as typical of the reduction of the diamond results:—

	No. of experiments.	Range of temperature.	Weight in grammes.	Volume of gas in c.c.	Specific heat.
Diamond ...	4	18° to Liquid air	1·901	271·5	S. H. = $\frac{1·164}{1·901} \times \frac{271·5}{106} \times 0·0295$ = 0·0463.
Lead	2	" "	1·164	106·0	
Diamond ...	2	Solid carbonic to Liquid air	1·729	54·0	S. H. = $\frac{0·50}{1·729} \times \frac{54}{23·5} \times 0·029$ = 0·0193.
Lead	1	" "	0·500	23·5	
Diamond ...	3	Liquid air to Liquid hydrogen	2·142	58·5	S. H. = $\frac{1·996}{2·142} \times \frac{58·5}{351} \times 0·0280$ = 0·00435.
Lead	4	" "	1·996	351·0	

The mean results of the experiments made with diamond, graphite, and ice, are given in Table I. In the second column the number of experiments is given; the third column specifies the range of temperature through which the substance fell in giving up its heat at the lower temperature; the fourth column contains the mean specific heat of the substance calculated by comparison with that of lead, each separate experiment being compared with an immediately preceding or succeeding experiment with lead.

Table I.—Specific Heats.

Substance.	No. of experiments.	Range.	Specific heat.
Diamond	17	Liquid air to 18°·5	0·04727
	8	Liquid air to solid carbonic acid ...	0·01905
	3	Liquid hydrogen to liquid air	0·00435
Graphite	1	Liquid air to 19°·5	0·0948
	2	Liquid air to solid carbonic acid ...	0·0599
	2	Liquid hydrogen to liquid air	0·0133
Ice	3	Liquid air to -18°	0·348
	8	Liquid air to solid carbonic acid ...	0·285
	2	Liquid hydrogen to liquid oxygen	0·146

From these results are constructed the following summary of specific heats :—

Table II.

Substance.	18° to -78°.	-78° to 188°.	-188° to -252°·5.
Diamond	0·0794	0·0190	0·0043
Graphite	0·1341	0·0599	0·0133
Ice	0·463*	0·285	0·146

It appears from these values that between the ordinary temperature and the boiling point of hydrogen the specific heat of the diamond has been reduced to 1/19, whereas under similar conditions graphite has diminished to about 1/10. Further it will be observed that at the lowest temperatures the specific heat of graphite is about three times that of the diamond. It is also worthy of being recorded that the values of the specific heats of diamond and graphite taken between the temperature of liquid air and boiling hydrogen are far smaller than that of any known solid substance, being even lower than that of any gas taken under constant volume.

Early determinations of the specific heat of carbon in any of its forms showed complete departure from the law of Dulong and Petit. But all such experiments were in general made over a range of temperature from about the freezing point of water to some two or three hundred degrees Centigrade. In April, 1872, Professor H. F. Weber read a paper on the specific heat of carbon before the Chemical Society of Berlin. I had made experiments on the same subject for the purposes of a paper read on April 1 of the same year before the Royal Society of Edinburgh, a continuation of which was read to the British Association in the following August. Both of these papers appeared in the 'Philosophical Magazine' of 1872.†

Professor Weber's observations extended from 0° to 200°, and led him to the conviction "that the specific heat of carbon in all its allotropic modifications varies to a considerable degree with the temperature." This he verified by finding that "the specific heat of the diamond is tripled when the temperature is raised from 0° to 200°." My own investigations at that time consisted of two groups, the first from 20° to the boiling point of zinc, taken

* This is from -18° to -78° in the Ice experiment.

† H. F. Weber, "The Specific Heat of Carbon," 'Phil. Mag.,' 1872, ser. 4, vol. 44, p. 251; J. Dewar, "The Specific Heat of Carbon at High Temperatures," 'Phil. Mag.,' vol. 44, p. 461.

as 1040° C., and the second to the temperature of the oxy-hydrogen blow-pipe, some 2000° C. I found that the mean value of the specific heat of gas-carbon in the first range was 0·32, and for the second range was 0·42, and I added "the true specific heat at 2000° must be at least 0·5; so that at this temperature carbon would agree with the law of Dulong and Petit." In 1875* Professor Weber published results, proceeding by a series of intermediate steps up to 1000°, and showing finally "that from the point (about 600°) at which the specific heat of carbon ceases to vary with increase of temperature, and becomes comparable with that of other elements, any real difference in the specific heats of the two modifications disappears, and carbon obeys the law of Dulong and Petit."

Professor Weber further showed that the specific heat of carbon, in both its forms, when plotted to temperature as abscissa, produced a curve with a point of inflection in it, like the Old English *f*. He found† the point of inflection at about 60° C. for diamond and at about 0° C. for graphite. The results given by Weber lead to the Table.

Table III.

Substance.	Range.	Specific heat.
Diamond	-79°·7 to +21°·4	0·0806
Graphite	-79°·3 to +21°·6	0·1301

The close agreement between the result of the present investigation for diamond and Weber's over the same range, using the Bunsen ice calorimeter, is noteworthy; the slight divergence in the case of graphite may easily be accounted for by the difference in the graphites used. But in both cases the present results coincide with the trend of the curve as pointed out by Weber for low temperatures. The Weber formula for the diamond, namely,

$$\text{Specific heat} = 0\cdot0947 + 0\cdot000994t - 0\cdot00000036t^2,$$

if extrapolated, would make the specific heat of diamond vanish about -92° C. Behn‡ gives the specific heat of graphite between -78° and -186° as 0·075, which is much higher than the value given in Table II.

* 'Phil. Mag.,' 1875, ser. 4, vol. 49, p. 285.

† 'Phil. Mag.,' vol. 49, pp. 180, 279.

‡ 'Ann. der Phys.' (1900), ser. 4, vol. 1, p. 261.

Previous observations on the specific heat of ice are few, but the following have been noted :—

Regnault.....	−78 to 0	0.4627
Person.....	−30 „ 0	0.505
Person.....	−21 „ −1	0.5017

These are in agreement with the first result for ice in Table II.

The specific heat of ice between the temperatures of liquid air and liquid hydrogen has practically been reduced to about 1/3 the value between 0° and −78°, and has finally only about half the specific heat of steam at constant volume.

It would be a matter of interest to investigate the general behaviour of various groups of substances, as regards their specific heats at low temperatures, and without having attempted any careful systematic investigation, the following observations extracted from laboratory records are fairly representative of some classes of bodies. In Table IV the specific heats of two alloys

Table IV.

No. of obs.	Substance.	Weight used in grammes.	Range of temperature. Degrees Centigrade.	Vol. of gas in cubic centimetres.	Sp. heat.
1	German silver	0.22	− 18 to −188	48	0.080
1	Brass	0.627	+ 19.5 −188	166	0.099
1	0.244	−188 −252.5	66 (H)	0.043
2	Tellurium	0.645	+ 18.2 −188	99.5	0.047
2	Sulphur	0.289	+ 18.2 −188	131	0.137
2	Selenium	0.353	+ 18.2 −188	80	0.068
2	Potassium alum.....	0.180	+ 18.8 −188	152.5	0.256
2	0.376	− 78 −188	130	0.223
2	Chromium alum.....	0.20	+ 20 −188	162	0.243
2	0.392	− 78 −188	135	0.222
1	Calcium chloride (hydrate)...	0.184	+ 20 −188	180	0.294
1	0.336	− 78 −188	141	0.271
3	Sodium chloride.....	0.105	+ 16 −188	55.2	0.187
2	0.253	− 78 −188	65.5	0.164
3	Ammonium chloride.....	0.064	+ 16 −188	45.8	0.300
2	0.130	− 78 −188	42.5	0.207
2	Naphthaline	0.55	+ 16 −188	31.5	0.202
2	0.105	+ 16 −188	57.25	0.194
1	0.090	+ 15 −188	50.5	0.204
2	0.203	− 78 −188	40.6	0.126
1	Paraffin	0.08	+ 15 −188	68.5	0.312
1	0.105	− 78 −188	38.5	0.176
1	Silver iodide	0.307	+ 16 −188	44.5	0.062
2	„ bromide	0.196	+ 16 −188	35.5	0.064
2	„ chloride	0.215	+ 16 −188	49.75	0.082
5	Solid carbonic acid	0.164	− 78 −188	57.1	0.215
1	0.15	− 78 −182.5	50	0.225
1	0.190	− 78 −182.5	62	0.223
2	Solid ammonia	0.14	−103 −188	72.25	0.519
2	0.156	−103 −188	77.5	0.460
3	Solid sulphurous acid	0.325	−103 −188	75.2	0.228
3	0.311	−103 −182.5	57.3	0.226
2	Ceylon thoria mineral	0.500	+ 15 −188	70.6	0.044

are given, which were used in the course of the present investigation; also those of the group of sulphur, selenium, and tellurium. Two alums, for which Kopp had made some observations, were included in the research, together with three other typical salts. Again, naphthaline and paraffin were a pair, whose specific heats were examined; also the chloride, bromide, and iodide of silver. The results for the solidified gases, carbonic acid, ammonia, sulphurous acid, were of obvious interest, and several observations on them are given. With regard to these bodies, it may be noted that the values found are not far removed from those of the specific heats at constant volume in the gaseous state, and I have no doubt that if the experiments had been extended to temperatures between that of liquid air and hydrogen these results would all have been below the gas constant. The other bodies examined all show diminution of specific heat at the lower temperatures, the most marked examples being the hydrocarbons, paraffin and naphthaline.

An almost endless field of research in the determination of specific heats and other thermal constants is now opened, in which liquid air and hydrogen calorimeters are certain to become ordinary laboratory instruments.

II.—*Latent Heats.*

(Received June 5,—Read June 8, 1905.)

In the course of my experiments on the specific heat of diamond, graphite, and ice by means of the liquid hydrogen and air calorimeters, the frequent determination of the quantities of gas evaporated by lead in the same circumstances as the diamond, graphite, or ice under investigation afforded means for the direct measurement of the latent heats of hydrogen, nitrogen, oxygen, and air at their respective boiling points. The same data for lead* were adopted as were used on the former occasion. The volumes of gas evaporated had, however, to be reduced to 0° C. and 760 mm. of pressure. If C be the number of cubic centimetres of gas evolved per gramme of lead, measured at 0° C. and 760 mm., while the lead cools from t'° to t° , m the number of grammes mass of gas per cubic centimetre under standard conditions, and s' the mean specific heat of lead between t'° and t° , then L the latent heat of the gas is given by

$$L = \frac{t' - t}{mC} s'.$$

* Behn ('Ann. d. Physik,' 1900, IV, 1, p. 261) gives sp. heat of lead as 0.0300 from 18° to -79°, and 0.0291 from -79° to -186°, whence we get 0.0295 from 18° to -186°. From 100° to 18° he gives the value 0.0310, but adds that this is the "mean of known results." Later Schmitz ('Roy. Soc. Proc.,' 1903, vol. 72, p. 192) gives the sp. heat of lead as 0.0293 at -85°, and 0.0305 at +60°.

The subjoined table contains a summary of the results obtained :—

Substance.	No. of expts.	Fall of temp.	Latent heat.	Mean.
Oxygen	6	17° to -182°·5	51·72	} 51·15
	3	16·4 -182°·5	51·06	
	5	-78 -182°·5	50·65	
Nitrogen	3	18·4 -195°·5	50·4	} 50·4
	4	17 -195°·5	48·1	
	4	-78 -195°·5	52·7	
Hydrogen	5	17 -252°·5	122·9	} 123·1
	4	17 -252°·5	123·6	
	4	-188 -252°·5	124·3	
	6	-188 -252°·5	121·5	

The following details of three sets of observations show how closely the results are in accord :—

Oxygen.—From -78° to $-182^{\circ}\cdot 5$; Bar., 760·9 mm. ; temp., $16^{\circ}\cdot 4$.					
Weight of lead in grammes.	Volume of gas in cubic centimetres.	Cubic centimetres of gas per gramme of lead.	Mean.	Reduced to 0° C. and 760 mm.	Latent heat.
1·529	67	43·83	} 44·30	} 41·84	$L_O = \frac{104^{\circ}\cdot 5 \times 0\cdot 0290}{0\cdot 00143 \times 41\cdot 84} = 50\cdot 65$
1·508	67	44·58			
1·545	68	44·01			
1·431	64	44·73			
1·567	69	44·35			
Nitrogen.—From $18^{\circ}\cdot 4$ to $-195^{\circ}\cdot 5$; Bar., 760 mm. ; temp., $18^{\circ}\cdot 4$.					
0·471	50	106·2	} 106·3	} 99·59	$L_N = \frac{218^{\circ}\cdot 9 \times 0\cdot 0295}{0\cdot 001257 \times 99\cdot 59} = 50\cdot 41$
0·641	68	106·1			
0·657	70	106·5			
Hydrogen.—From $16^{\circ}\cdot 4$ to $-252^{\circ}\cdot 5$; Bar., 753 mm. ; temp., $16^{\circ}\cdot 4$.					
0·160	117	731·2	} 760·5	} 710·8	$L_H = \frac{268^{\circ}\cdot 9 \times 0\cdot 0291 \times 1000}{0\cdot 0696 \times 710\cdot 8} = 122\cdot 92$
0·147	116	789·0			
0·122	94	770·5			
0·147	112	761·9			
0·104	78	750·0			

The latent heat of hydrogen, determined from 19 observations—some through the short fall of temperature from liquid air, some through the much larger fall from ordinary temperatures—may be taken as very

closely 123 gramme-calories. Considering the great mobility of liquid hydrogen, and its small density, it might be imagined that some spray would get carried up by the hollow enclosing gas bubbles. If this took place in the experiments, then the latent heat would be too small. In like manner any solid air carried down from the neck of the calorimeter would have an effect of the same kind. If, however, the transit of the lead into the liquid hydrogen was impeded by a solid air constriction in the neck then the latent heat would be increased.

In my Bakerian Lecture,* the latent heat of hydrogen was taken to be about 200 units, from which I made the following deduction:—"The order of the specific heat of liquid hydrogen has been determined by observing the percentage of liquid that has to be quickly evaporated under exhaustion in order to reduce the temperature to the melting point of hydrogen, the vacuum vessel in which the experiment is made being immersed in liquid air. It was found that in the case of hydrogen the amount that had to be evaporated was 15 per cent. This value, along with the latent heat of evaporation, gives an average specific heat of the liquid between freezing and boiling point of about 6." The present investigation enables me to correct this statement, the specific heat of the liquid between the boiling and the freezing point in reality being 3·4 instead of 6. It appears, therefore, that hydrogen, instead of following the law of Dulong and Petit, has even in the liquid state an atomic heat of only half the required amount. In my paper on "The Physical Constants of Hydrogenium,"† it was shown that the specific heat of hydrogen absorbed in palladium was about 3·5. It seems therefore that hydrogen in the gaseous, the occluded, and the liquid condition, has substantially the same specific heat.

In the Bakerian Lecture,‡ I noted for comparison with the specific heat of liquid hydrogen that when liquid nitrogen was similarly treated, "the resulting specific heat of the liquid came out 0·43, or about 6 per atom." Alt,§ in a recent direct determination of this quantity, gives the value 0·430. This corroboration of the old determination of the specific heat of liquid nitrogen got by the evaporation method, tends to confirm the accuracy of the value now found for the similar constant for hydrogen.

Further corroboration of this value of the latent heat of hydrogen is afforded by Clapeyron's equation,

$$\text{latent heat} = (v-u) t \frac{dp}{dt},$$

* 'Roy. Soc. Proc.' (June, 1901), vol. 68, p. 361.

† 'Trans. Roy. Soc. Ed.,' 1873.

‡ 'Roy. Soc. Proc.,' *loc. cit.*

§ 'Ann. d. Physik.' (April, 1904), IV, 13, p. 1027.

where v and u are the specific volumes of the gas and the liquid at temperature (absolute) t and pressure p . With this equation we must combine either a Rankine or a Willard Gibbs relation between vapour pressure and temperature. From some early observations with the helium thermometer on the vapour pressure of hydrogen below its boiling point, I found the Rankine equation

$$\log p = 5.5038 - \frac{53.13}{t}.$$

Hence, noting that the density of liquid hydrogen at the boiling point is 0.07, and the specific volume of the gas at the same temperature is about 818.7 c.c., Clapeyron's equation gives 120.3 as the latent heat of liquid hydrogen.

A corresponding mean Rankine formula, based on Travers'* smoothed results, gave the latent heat as 119. On the other hand, two Willard Gibbs' equations, calculated from actual observations as evenly distributed as possible, gave the results 123.4 and 117.5, or a mean of 120.5. Thus, while theoretical results seem somewhat lower than those of observation, both point to a value of the latent heat of hydrogen about 121 or 122 gramme-calories.

In the case of nitrogen the observations seem equally good, and we get its latent heat about 50.4 gramme-calories. Determinations of this quantity by former observers are in very fair accord with this value. A careful investigation by Fischer and Alt† gave 48.9, and more recently Alt‡ gives 48.7 at 718 mm. pressure ($-196^{\circ}2$) and 52.07 at 96 mm. pressure ($-210^{\circ}05$). Again, Shearer§ found in two series of experiments the slightly higher value 49.8, a result (he says) which "agrees very well with that computed from the vapour tension which gives 49.25."

From observations of my own on the vapour density of nitrogen between the boiling and melting points, I deduced a Rankine formula,

$$\log p = 6.6462 - \frac{292}{t},$$

which leads to 48.03 for the latent heat of the liquid. In similar circumstances from Fischer and Alt's results, I find the value to be 49.65, while a Willard Gibbs formula from the same observations gives 51.4. The ratio of the liquid to the gaseous volume at the boiling point being only 1/177, the correction on this account may be neglected in using Clapeyron's equation.

* 'Phil. Trans.' (1902), A, vol. 200, p. 169.

† 'Ann. d. Physik.' (1902), IV, 9, p. 1180.

‡ 'Ann. d. Physik.' (1904), IV, 13, p. 1024.

§ 'Phys. Rev.' (1903), vol. 17, pp. 124, 471.

The value of the latent heat of oxygen is found to be 51.15 gramme-calories, the result of 14 observations, with a possible divergence of half a calorie either way.

Among the most recent determinations of the latent heat of oxygen, Shearer* gives the results of two series of observations as 60.9 and 61.0, and adds 60.8 as the result of "thermodynamic computation." Estreicher,† by an electric method, finds this quantity to be 58 calories per gramme. These results are so high compared with other determinations that they must be received with some caution. A direct and careful series of observations by Alt,‡ also by an electric method, gives 52.07 as the latent heat of oxygen at $-182^{\circ}.8$ (pressure 725 mm.), rising to 58.85 at $-201^{\circ}.3$ (pressure 68 mm.).

Olzewski, Estreicher, and Travers have made observations on the vapour density of oxygen which enable us to calculate its latent heat. Three Willard Gibbs' equations were calculated from Olzewski's§ observations between the critical point and the boiling point, from which a mean value of 51.4 was found. A careful examination and selection from Estreicher's|| three sets of observations between the boiling and the melting point led to a Willard Gibbs equation, from which the latent heat was found to be 52.53. From Travers¶ smoothed results a series of six Rankine formulæ was calculated between $90^{\circ}.7$ and $79^{\circ}.17$ (absolute), from which the mean value of the latent heat was found to be 53.78. The ratio of the liquid to the gaseous volume of oxygen at its boiling point being only 1/255, its effect in the Clapeyron equation may be neglected.

As between oxygen and nitrogen it would appear that the former has the greater latent heat, a result to be expected if we rely on the constancy of Trouton's constant, namely, that the molecular latent heat is proportional to the absolute temperature of the boiling point. We may determine the ratio of these two latent heats independently of the value of the specific heat of lead, by selecting observations over approximately the same range of temperature, for we have noted how slight is the variation of the specific heat of lead per degree of temperature. On examining the details of the possible sets of observations that may be compared, I select the set for

* 'Phya. Rev.' (1903), vol. 17, pp. 124, 469—475.

† 'Acad. Sci. Crac.' (1904), Bull. 3, pp. 183—186; 'Sci. Aba., June, 1904 ("Physica, No. 1441.

‡ 'Ann. d. Physik.' (1904), IV, 13, p. 1020.

§ 'Comptes Rendus' (1885), vol. 100, p. 351; 'Nature' (1895), vol. 51, p. 355; 'Phil. Mag.' (1895), vol. 40, p. 210.

|| 'Phil. Mag.' (1895), vol. 40, pp. 458, 459.

¶ 'Phil. Trans.' (1902), A, vol. 200, p. 152.

nitrogen in which a mean of 106.3 c.c. of gas per gramme were given off. This, reduced to 0° and 760 mm., became 99.59 c.c., over a range of temperature from 18°.4 to -195°.5. Two sets of oxygen observations seem equally good, namely, the first two. In the former of these the mean volume of gas given off per gramme, reduced to 0° and 760 mm., was 79.38 c.c., over a range of temperature from 17° to -182°.5; and in the latter 80.34 c.c. were given off in the same standard circumstances over a range from 16°.4 to -182°.5.

Combining these last two with their relative weights of 6 and 3, we get, putting s' for the specific heat of lead, and w for the weight of 1 c.c. of hydrogen,

$$L_O = \frac{198°.9 + 2 \times 199°.5}{(80.34 + 2 \times 79.38) \times 16w} s'$$

while from the nitrogen observations we have

$$L_N = \frac{213°.9}{99.59 \times 14w} s'.$$

Hence
$$\frac{L_O}{L_N} = \frac{597°.9 \times 99.59 \times 14}{213°.9 \times 239.10 \times 16} = 1.019.$$

This result confirms us in the view that the latent heat of oxygen is greater than that of nitrogen.

Similar ratios between the latent heats of hydrogen and oxygen and hydrogen and nitrogen are of importance in themselves, having regard to future work, and even although the ranges of temperature may not be coincident, nevertheless the change in the value of the specific of lead will not affect the ratios by much more than about 1 per cent., supposing we take the specific heat of lead to be the same in both.

Thus, taking two of the longest ranges for temperature, namely, hydrogen from 17° to -252°.5 and oxygen from 17° to -182°.5, we get the ratio

$$\frac{L_H}{L_O} = \frac{16 \times 79.58 \times 269°.0 \times 0.0291}{1 \times 710.78 \times 199°.5 \times 0.0295} = 2.38;$$

similarly, taking two short ranges, namely, hydrogen from liquid air and nitrogen from solid carbonic acid, we find

$$\frac{L_H}{L_N} = \frac{14 \times 51.46 \times 64°.5 \times 0.0280}{1 \times 162.22 \times 117°.5 \times 0.0290} = 2.35.$$

From the former of these with $L_O = 51.15$, we get $L_H = 121.7$; and from the latter with $L_N = 50.4$, we get $L_H = 118.4$.

The latent heat of air is a quantity whose determination is of a different order from that of either oxygen or nitrogen, seeing that the liquid evaporated

is not always of the same composition, and the composition has not always been noted. Behn* made a determination of it and found its value to be 50·8 gramme-calories. But in dealing with this value later in his paper, he takes the composition of the liquid air employed as containing 93 per cent. of oxygen. This result may, therefore, be more appropriately used as a lower limit to the latent heat of oxygen, and thus far as a corroboration of the present value found for oxygen. D'Arsonval† states, without giving any details, that he found the latent heat of air to be 65 calories. Shearer‡ has examined this quantity carefully on two occasions, using the same method each time. He distinguishes clearly the effects of various compositions. In his earlier series of experiments he found that for air containing from 21·8 to 72 per cent. of oxygen, the latent heat varied from 44·02 to 51·7 gramme-calories. In his later series, he found that for air containing from 48 to 90 per cent. of oxygen, the latent heat rose from 50·6 to 59 gramme-calories. Still more recently Fenner and Richtmyer,§ employing Shearer's method, find that from about the composition of atmospheric air until the mixture contains about 94 per cent. of oxygen the latent heat remains apparently constant at 50·966, and that then it appears to rise rapidly to 54·10 at 97·6 per cent. of oxygen. They seem to accept 61 gramme-calories as the latent heat of oxygen, so that the increase from 97·6 per cent. to 100 per cent. is exceptionally rapid.

In the present series of observations, the liquid air employed was *old*, that is, it was very rich in oxygen. If therefore we take the density of the air in the gas-receiver as being equal to that of oxygen, we shall have values of the latent heat of liquid air erring by defect. In the earliest experiment the volume of gas given off was (at 0°, and 760 mm.) 84·25 c.c. per gramme of lead, from 18°·5 to -184°·5, whence

$$L_{\text{air}} = \frac{0.0295 \times 203^{\circ} \times 1000}{84.25 \times 1.43} = 49.7.$$

Similarly in a later case from 17°·9 to -188°, the volume per gramme of lead was (at 0°, and 760 mm.) 79·54 c.c., whence $L_{\text{air}} = 53.41$. After this, several series of experiments were made in which a succession of half-grammes of lead, 10 or 12 at a time, were dropped into old liquid air. In one experiment where 12 half-grammes were employed, the mean volume of gas given off per gramme was (at 0°, and 760 mm.) 76·52 c.c., and the range of temperature was

* 'Ann. d. Physik' (1900), IV, 1, p. 271.

† 'Comptes Rendus' (1901), vol. 133, p. 983.

‡ 'Phys. Rev.' (1902), vol. 15, p. 191; (1903), vol. 17, p. 472.

§ 'Phys. Rev.' (1905), vol. 20, p. 81.

from $10^{\circ}9$ to -188° , thus giving the latent heat of air as 53.63. These last values come very near those found by Fenner and Richtmyer; but the results are so varied that it is clear the question of the latent heat of air of very high oxygen-concentration is one requiring further investigation.

Explosions of Mixtures of Coal-Gas and Air in a Closed Vessel.

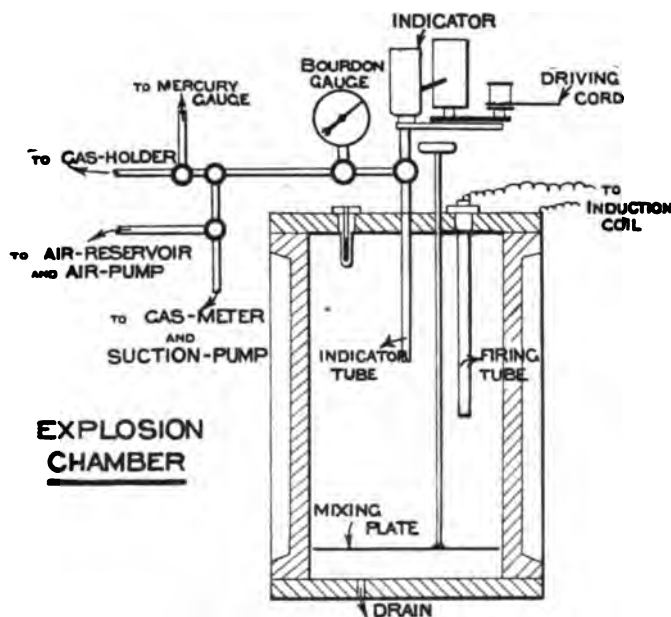
By LEONARD BAIRSTOW, A.R.C.Sc., Wh. Sch., and A. D. ALEXANDER, A.R.C.Sc., Wh. Sch.

(Communicated by Professor Perry, F.R.S. Received February 7,—Read March 9, 1905.)

(Abstract.)

The experiments were proposed by Professor Perry, and with his sanction and encouragement extended to more than two years' continuous work. The work had for its original object the determination of the explosive properties of compressed mixtures of coal-gas and air.

The main apparatus was designed by Messrs. McDiarmid and Mann, students of the Royal College of Science, South Kensington, and was made before the authors of this paper became connected with the work.



In the preliminary experiments it was found necessary to mix the gases independently of diffusion, and most of the experiments have consequently been made at an initial pressure of 35 lbs. per square inch absolute, as this allowed a considerable volume of air to be pumped into the cylinder after the coal-gas had been admitted. Eventually it was found necessary to take still greater precautions in special cases, and mechanical mixing was resorted to.

The figure shows the explosion cylinder, which was 18 inches long and 10 inches in diameter internally. The records were taken with an ordinary indicator, the spring being usually 150 lbs. per square inch per inch. The recording drum was made to revolve continuously at a speed giving 42.5 inches of diagram per second. By varying the firing arrangements the mixtures could be ignited at different points, and a further deviation from previous work was made by altering the length of the tube which led to the indicator. The firing tube shown in the figure was closed at the top where the spark was produced, and communication with the cylinder took place through a pin-hole near the bottom. The proportion of coal-gas to air was kept constant, and using the above tube the mixture was fired at different points. In general, changes resulted both in the time of explosion and in the maximum pressure.

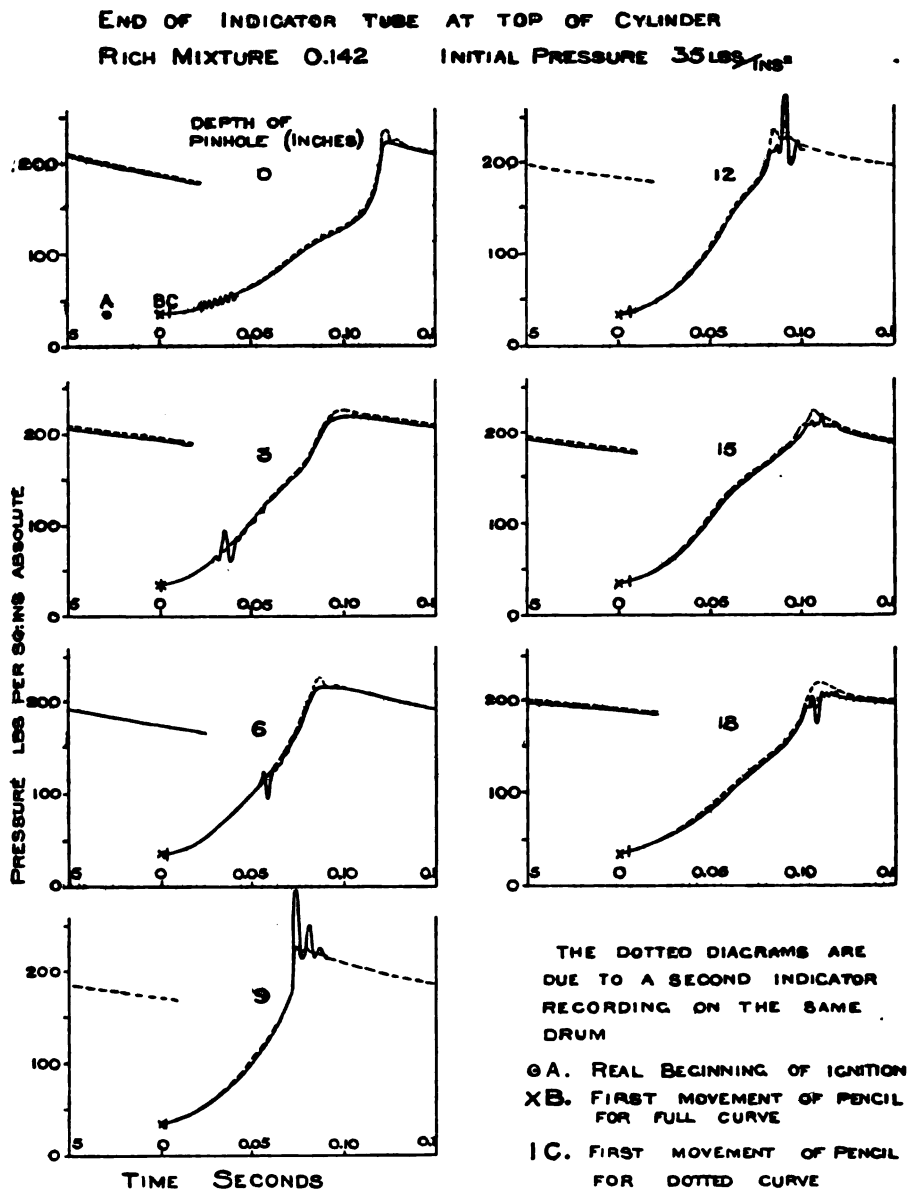
For the most explosive mixture the change in the maximum pressure was small (fig. 8 of original paper), being only of the order of 1 per cent., but in weak mixtures the variations sometimes exceeded 30 per cent. Such differences can only be observed in a vessel which absorbs heat, but it does not thereby follow that the differences are entirely due to the heat lost by the gases before the highest pressure is reached, since the maximum pressure does not coincide with the end of combustion when the rate of cooling approaches the rate of reception of heat by explosion. This and the cooling loss can be differentiated in some of the diagrams obtained, and the experiments were used as a guide to correction.

Convection currents were also indicated by the method of firing, by explosions starting at the bottom of the cylinder being quicker than an otherwise similar one beginning at the top. The currents are sometimes very considerable.

In order to reduce the cooling effects, the explosion was often commenced at four points in the axis of the cylinder. The four spark-gaps were in one continuous circuit, and the sparks, therefore, occurred simultaneously. Keeping the initial pressure constant the mixture was varied. The highest pressure and the most rapid explosion was produced when the oxygen of the air was just completely burnt. The pressure fell continuously as the pro-

342 Messrs. Bairstow and Alexander. *Explosions of* [Feb. 7,
 portion of coal-gas to air was diminished, until the fractional volume of the
 mixture occupied by the coal-gas was about 1 in 12. A sudden change then

FIG. 8.



occurred, and combustion remained incomplete after explosion. Mixtures
 between 1 in 12 and 1 in 17 were still explosive, but the amount of gas burnt

decreased, at first suddenly and then regularly until the limit of inflammability was reached.

If then, the gases remaining in the cylinder, after an explosion of a mixture less rich in coal-gas than 1 in 12 were used instead of air in a subsequent explosion, higher pressures should result. This was observed to be the case, and with a necessary modification furnishes the explanation of the experimental results obtained by Mr. Grover in 1895.*

In the diagrams of fig. 8 ripples are shown between the beginning of explosion and the time at which the maximum is reached. It is obvious from their position that they are not due to the inertia of the indicator. With four sparks or a single spark at the top of the cylinder these occur early in the diagram, and are not usually very noticeable. When, however, the point of firing is altered, the change is accompanied by a difference in the position of the ripples. A measurement of them, when sufficiently uniform to be measured, showed that the period was independent of the pressure at which they occurred, and eventually they were traced to sound waves in the indicator tube produced by the arrival of the flame at its open end. All the observed conditions are then satisfied. Supposing then that the end of the indicator tube is in the upper surface of the cylinder (as in the cases of fig. 8), and that the mixture is fired below the middle of the cylinder, the flame will reach the bottom first and explosion will be completed when the ripples occur, that is they will occur on the top of the diagram, as in the figure. The conclusion as to their cause was confirmed by altering the length of the indicator tube and noting the change produced in the position and period of the ripples.

When the ripples occurred at the maximum pressure the amplitude was sometimes enormous, the extra pressure due to the ripples being often as great as the pressure due to combustion in the cylinder. This phenomenon is probably connected with the detonation wave investigated by MM. Mallard and Le Chatelier† and by Professor H. B. Dixon.‡ There is no evidence of the detonation wave in the cylinder itself in any of our experiments. The big movements are never found with weak mixtures, or even in rich mixtures fired with short tubes.

With weak mixtures, even when combustion is complete after explosion, the ripples indicate that the flame travels through the more inflammable portions of the mixture first, and therefore that the constituents burn

* "Modern Gas and Oil Engines," Grover.

† 'Ann. des Mines,' 1883.

‡ 'Phil. Trans.,' A, 1903.

successively. This type of combustion can be detected until the coal-gas occupies more than one-eighth of the volume of the mixture.

As explosion begins very slowly, a small amount of friction in the indicator introduced an appreciable error in the time of explosion. This was estimated by making an external gap in the spark circuit which included the indicator paper. By this means a hole was pierced in the paper at the time of sparking and (fig. 8) shows the amount of error in a particular case. (The necessary corrections are given in the full paper, which is preserved in the Archives of the Royal Society.)

Experiments on Compressed Mixtures.

These experiments form an extension of the work of Mr. D. Clerk in 1886.*

The arrangement of four sparks was found to produce the most consistent results, and it was then noticed that slight changes in the composition of the coal-gas affected the experiments, particularly the rate of cooling. To make comparative experiments, therefore, it is necessary to do them at the same time and on the same gas. Three series are given, each the result of one day's experiments. The gas used in the first two is the same, but different to that used in the third series.

Series 1 (fig. 11).

Mixture constant (volume of coal-gas divided by the volume of air = 0.168). Initial pressure varied from $\frac{1}{2}$ to 3 atmospheres.

Series 2 (fig. 12).

Mixture constant (0.105). Initial pressure as in Series 1.

Series 3 (fig. 13).

Initial pressure constant. Mixture varied.

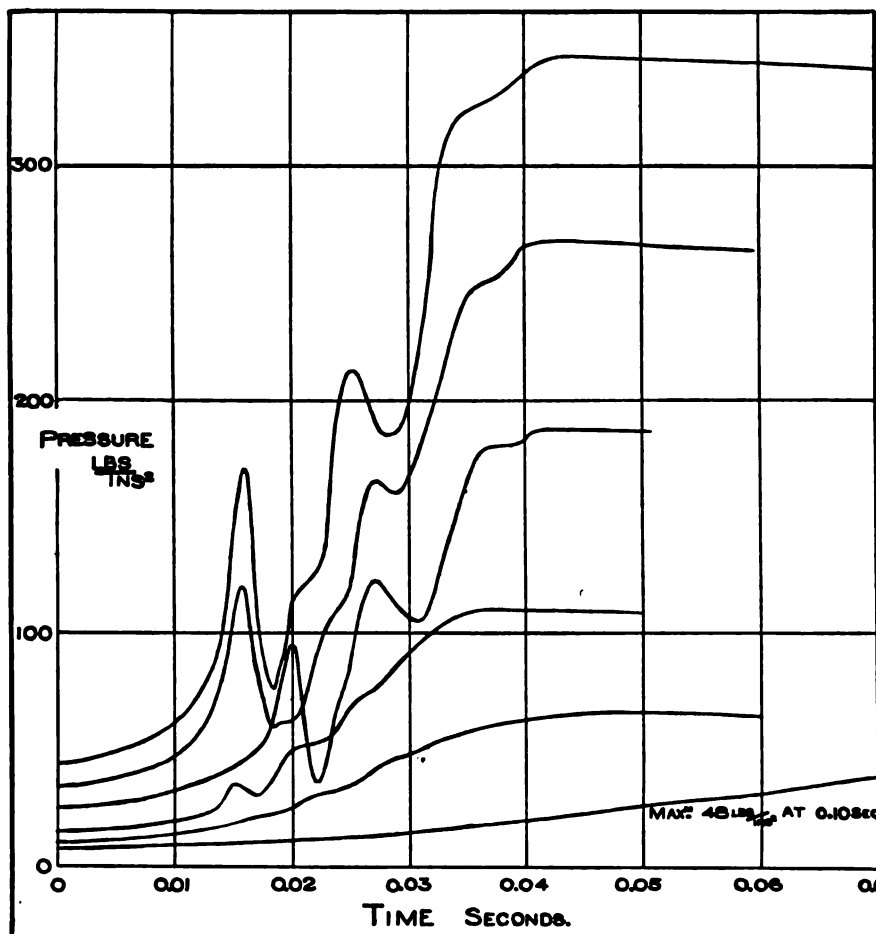
(Tables accompanying these figures are given in the full paper.)

From fig. 11 it will be seen that for a mixture of 0.168 the time of explosion is almost independent of the initial pressure between one and three atmospheres, but considerable increase is noticed for the two lower pressures. Similarly, between the same limits the ratio of the maximum to the initial pressure is constant. With the weaker mixture the time of explosion increased as the initial pressure decreased, without any decided effect on the ratio of the maximum and initial pressures (fig. 12).

The mixtures for Series 3 are such that the volumes of coal-gas burnt

* 'Proc. Inst. Civil Eng.,' 1886.

FIG. 11.



increase in arithmetical progression. These experiments show clearly that the heating value of unit volume of coal-gas increases as the mixture gets weaker (fig. 13).

Fig. 14 gives the cooling curves for the three series. By analysing the curves it will be seen that the rate of cooling increases with increase of initial pressure, but is independent of the relative proportions of coal-gas and air.

Hypotheses Introduced in the Calculation of Explosive Phenomena.

The outstanding differences between calculated and experimental results can now be explained by dissociation or an increasing specific heat. The hypothesis of a specific heat increasing with temperature is based entirely, so

FIG. 12.

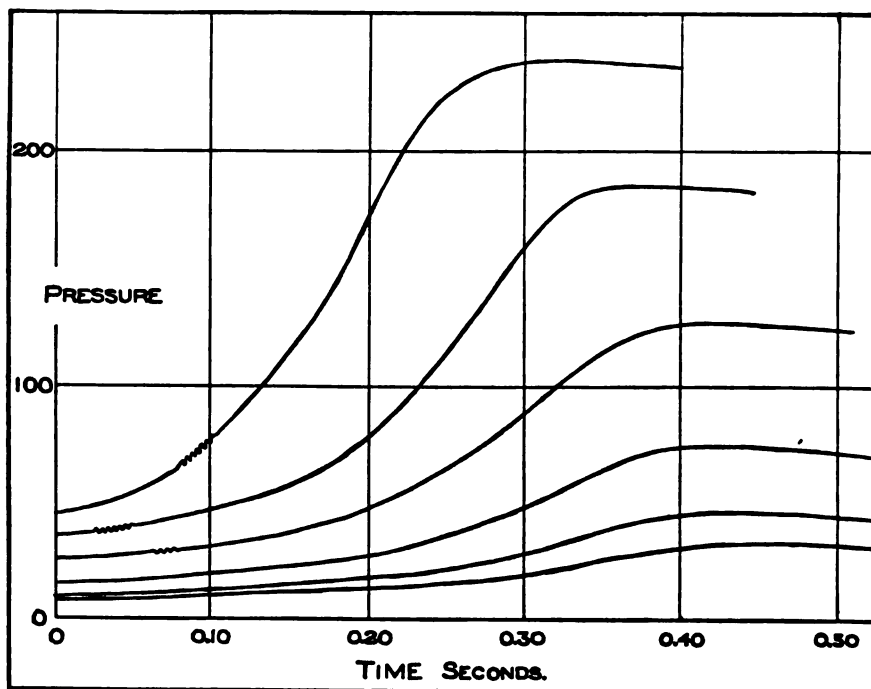
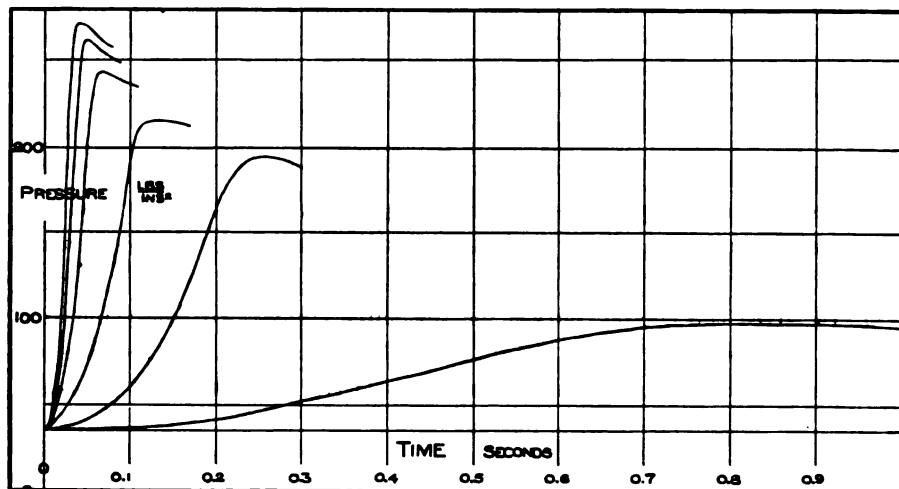
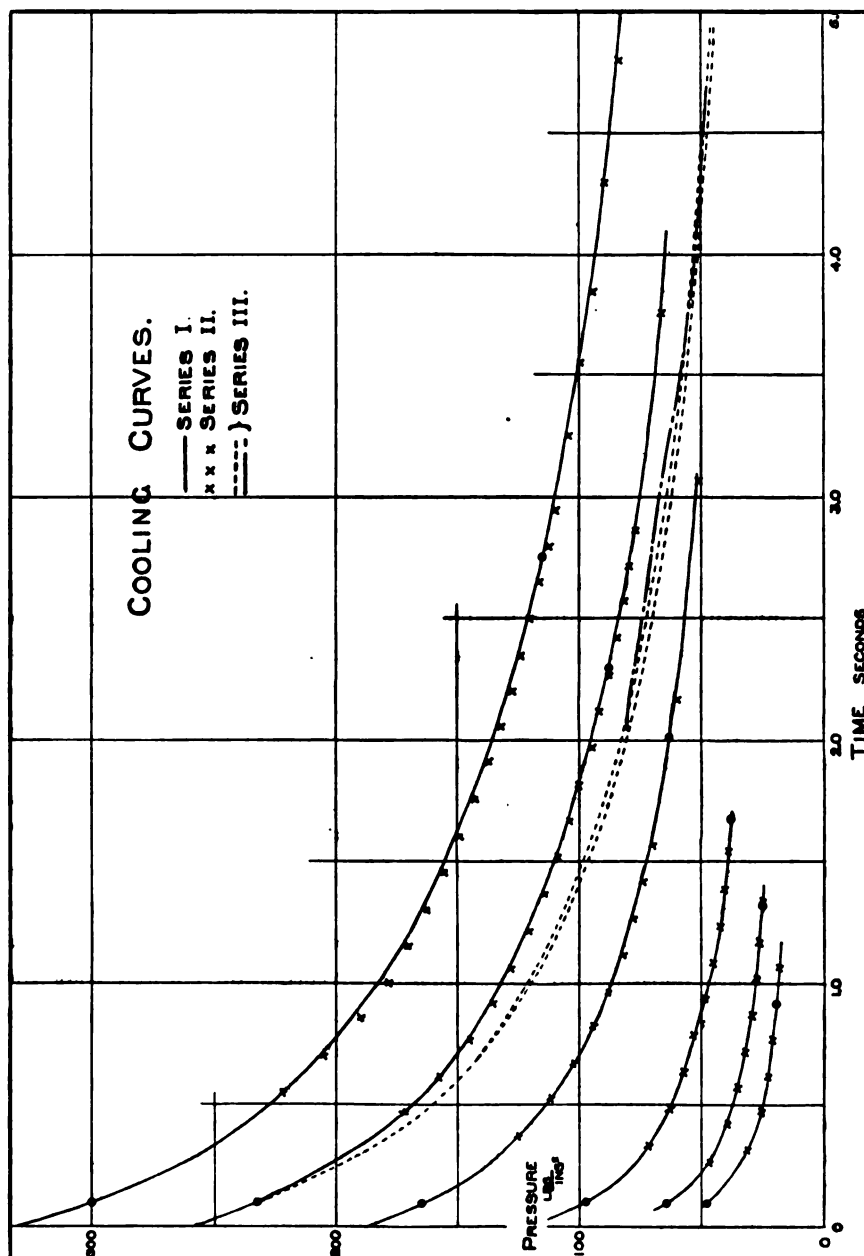


FIG. 13.



far as experimental evidence is concerned, on the work of MM. Mallard and Le Chatelier. They examined their cooling curves carefully in the search for a discontinuity at the lower limit of dissociation. Fig. 15 shows an analysis

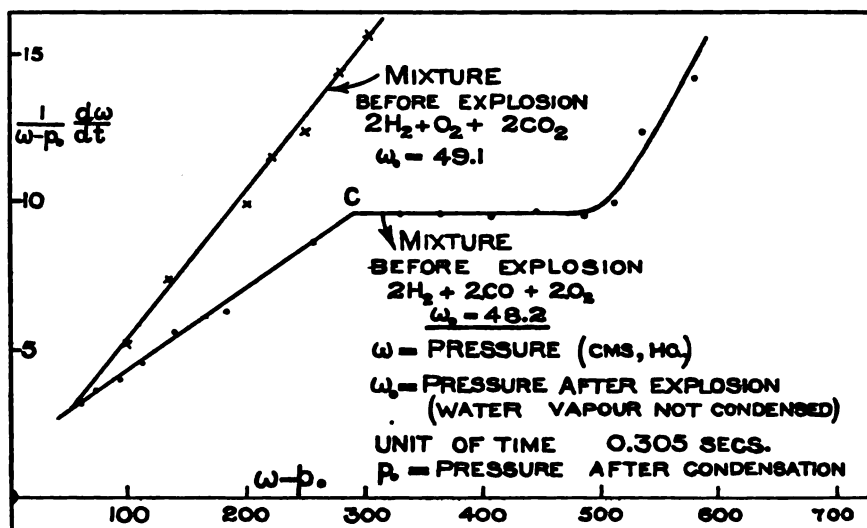
FIG. 14.



of two of their curves.* The lower curve shows the discontinuity in question at C. In both explosions concerned in diagram 15, the products are the same

* 'Ann. des Mines,' 1883.

FIG. 15.



both in composition and mass. In comparing results during cooling therefore, equal pressures mean equal temperatures. The rate of loss of pressure divided by the pressure is shown as the ordinate of the figure and the ratio of the two ordinates for any given abscissa, therefore gives the ratio of the rates of cooling in the two cases. Where $\omega - p_0$ is 300, the rate of cooling in one case is 50 per cent. greater than in the other.

The only apparent difference between two such cases lies in the maxima reached, and the only other experiments which afford any evidence on this point* agree in showing that the higher the maximum pressure and temperature, the lower the rate of cooling at any given subsequent temperature and pressure. The rise in the temperature of the cylinder walls would produce just such a change. A mathematical and experimental investigation showed that the metal itself does not increase in temperature greatly, and a film must therefore exist on the surface which sometimes attains a temperature of several hundred degrees Centigrade. Such a hypothesis satisfies all the observed experimental conditions, whilst it would be exceedingly difficult, if not impossible, to explain either the upper steep part of the curve in fig. 15, or the difference in the rates of cooling for the two cases, on the idea that C is the limit of dissociation.

Experiments at ordinary temperatures have not shown any such increase in specific heat as is necessary for the above hypothesis.

In order to determine the fraction of heat developed, the composition of

* 'Ann. des Mines,' 1883, p. 427.

the coal-gas and its calorific value were obtained. For the richest mixture (0.184 of coal-gas to 1 of air) the pressure obtained was 65.7 per cent. of that calculated. This fraction increased as the mixture was weakened, and was about 80 per cent. when combustion became incomplete. The highest temperature for the richest mixture is 2430° C. absolute, and the heat developed 63.2 per cent. On the hypothesis of increasing specific heat, the temperature would be 6 per cent. greater.

Summary.

Mixtures of coal-gas and air are not inflammable until the volume of coal-gas is greater than one-seventeenth of the combined volumes. Only a very small fraction of the gas then burns, the amount burnt rapidly increasing with increased richness of the mixture until the coal-gas is one-twelfth of the total volume. The least inflammable of the constituents then burns, and combustion becomes and remains complete so long as air is in excess. In these latter cases it is still probable that the constituents burn successively and not simultaneously.

The hypothesis of a specific heat increasing with temperature is not supported by direct experiment, and cannot be proved by any work on the pressures produced by explosion, the authors believing that a proof would require the measurement of temperature.

Direct experiments by Deville at temperatures below 1400° C. have shown that both steam and carbon dioxide are partially decomposed, and this dissociation is therefore taken by us as the sole explanation of the difference between the pressures calculated for explosions in a closed vessel and those actually obtained.

The Improved Electric Micrometer.

By P. E. SHAW, B.A., D.Sc.

(Communicated by Professor J. H. Poynting, F.R.S. Received March 30,—
Read April 13, 1905.)

I. Introduction.—The electric micrometer was first used for the measurement of the amplitude of a telephone diaphragm.* It was exhibited at the Royal Society Soirée in May, 1900. A succession of papers have followed in which the same principle has been applied to other measurements.† The apparatus used in these last papers is in every way an advance on the first one. It is described below for the first time.

The work done since 1900 has established the reliability of this method of measurement, and seems to show that the limit to its practical sensitiveness (a unit of 4×10^{-8} cm.) has been attained. It may be well, therefore, now to state in detail the form, peculiarities, and limitations of the apparatus.

II. The Instrument.—In the drawings fig. 1 is a side elevation of the micrometer and electric circuit; fig. 2 is an elevation, enlarged, showing details of the levers; fig. 3 is a cross-section on the line A'A', fig. 2; fig. 4 on the line B'B', fig. 2; fig. 5 is a section showing the contacts P, Q; fig. 6 is a diagrammatic view of the instrument and suspension.

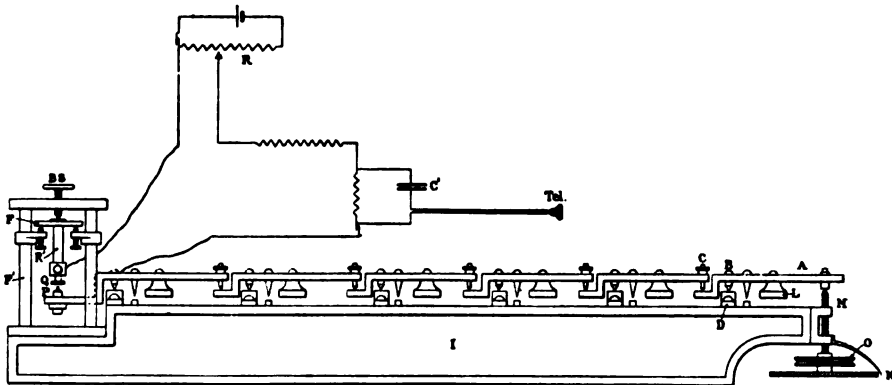


FIG. 1.

In fig. 1 are shown six levers of steel A fitted to turn on fulcrums B, the long arm of one lever being actuated by the short arm of the next through

* Shaw, 'Phys. Soc. Proc.,' vol. 17, and 'Phil. Mag.,' December, 1900.

† Shaw, 'Phil. Mag.,' 1901; Shaw and Laws, 'Electrician,' 1901 and 1902; Shaw, 'Roy. Soc. Proc.,' 1903; Shaw, 'Roy. Soc. Proc.,' 1904.

pointed pins C. The fulcrum blocks D, which are of hardened steel and have a true surface, are attached to the massive girder I of cast iron, and are surrounded by a metal casing E (fig. 2) which forms the sides of a bath for oil. The fulcrum are 1 inch wide, and rest only on two small knife-edges which are at the sides of the fulcrum as shown in fig. 4. The knife edges are of hardened steel.

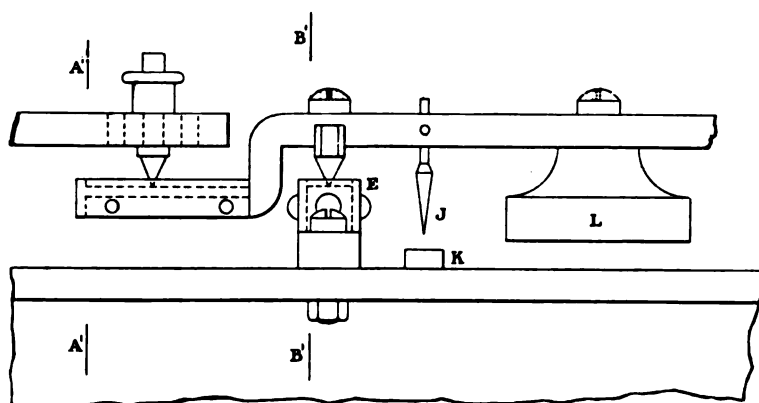


FIG. 2.

The short end of the levers are fitted with a hardened steel plate G (fig. 3), and with a metal casing H which forms the sides of a bath for oil. The pin C in the long end of the levers (except the first) is fixed by a nut, and the ends of the levers are provided with three holes for these pins so that leverage can be varied (see fig. 2).

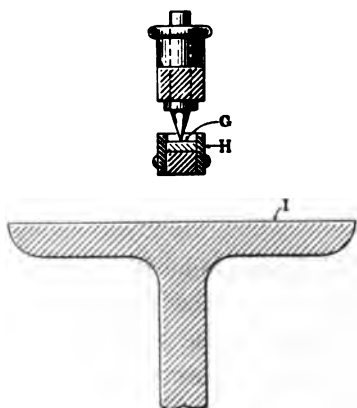


FIG. 3.

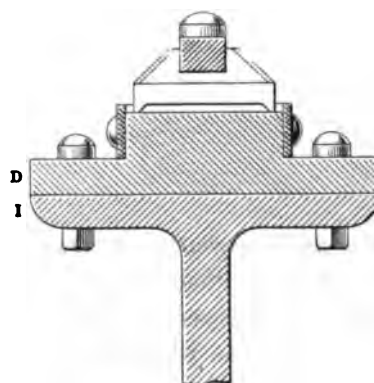


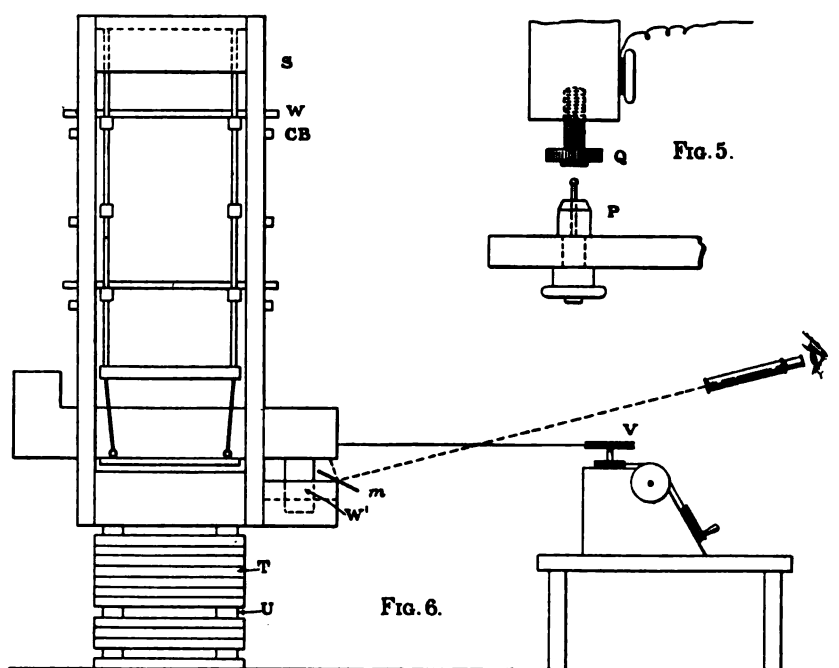
FIG. 4.

The levers are also fitted with pointers J, and the girder has index plates K by which the position of each lever can be fixed, or a template can be used between J and D for the same purpose.

Each lever is also provided with a weight *L* which gives firm pressure of the levers on the blocks and on one another.

The end of the long arm of the first lever is in contact by a polished agate plate with the point of the micrometer screw *M*, which has 20 threads to 1 cm., and whose nut is attached to the girder. The usual free nut and spring is used to reduce back-lash.

The lower end of the screw has a divided wheel *N* and a pulley *O*. The angular movement of the screw can be ascertained by watching in the telescope (fig. 6) the reflection in the mirror *m*, the under graduated face of *N*. The end of the last lever is fitted with a spherically-ended pin *P* (fig. 5) of iridio-platinum.



The fixed measuring surface *Q* is carried by a spindle *R'* from a plate *F* above, the position of which can be adjusted in the frame *F'* by the adjusting tripod screws shown at the side, and by the binding screw *BS* at the top. The whole frame and its attached parts are firmly fixed to the girder.

The instrument is enclosed in a felt-covered box, and is suspended by rubber springs from the top of a massive frame *S*, which itself rests on a pile of heavy concrete slabs *T* (2 feet square) with rubber cushions *U* at intervals. The tension of the springs may be adjusted by weights *W*, and

there are rails CB to prevent these weights falling on the micrometer in case of breakage.

The screw is actuated by an elastic cord driven by a pulley V which is on an independent table. To reduce the movement set up by the working of the pulley cord, the underside of the box has a plunger W' working in a dash-pot of castor oil.

The vertical movement of the screw actuates the system of levers, the extent of the movement being reduced by each lever in succession, and when the point P touches the fixed surface Q, an electric circuit is completed, and the telephone *tel.* sounds, as it also does when P and Q separate again.

The circuit shown includes a cell, potential divider R, high resistances telephone, and a condenser C'.

As regards dimensions, the height of fig. 6 is 10 feet and the parts are in proportion. The lever system is 3 feet long. Each lever is 6 inches long and is made of $\frac{1}{4}$ -inch square bar. The girder is 4 inches deep, and its material is $\frac{1}{2}$ -inch thick. The frame F' is small and massive for the sake of rigidity.

III. *Setting and Using.*—Suppose, as an example, we wish to find the magnetic expansion of the rod R' (fig. 1), *i.e.*, the amount it changes in length when a known current is sent through a solenoid of which R' is core.

Remove the plate Q, by unscrewing, and also the last lever which carries P. Polish P and Q with dry rouge on wash leather and finally with clean wash leather. Replace Q and the lever.

We have now to make P and Q come *just* into contact; this is a very delicate adjustment.

Put the telephone *tel.* to the ear. Adjust the three tripod screws and the binding screw BS on the top of the frame F'; the former work up and produce level while the latter works down. The whole system can be obtained rigid with P and Q just in contact, this contact being shown by the sounding of the telephone.

So far we have obtained only rough contact. To bring P and Q into *bare* contact, proceed to the pulley V (fig. 6) and wind the pulley cord, turning the screw M until the telephone sounds again.

This gives the *exact* position of contact. There will be a steady "creep" of the contact position for a considerable time after the covers have been put in place. Accurate work can be done when temperature equilibrium is established in, say, 15 minutes. The wheel N is watched and readings on it corresponding to the contact "make" and "break" are noted.

Change the magnetic field on R' by known amounts and note the corresponding changes in the contact positions of P, Q.

If the joint leverage come to 1000/1 and the screw pitch be 1/20 cm., with 500 graduations on N the unit of the instrument will be 10^{-7} cm.

IV. *Calibration*.—This can be done by measuring all the lever arms and multiplying the joint leverage into the unit of the micrometer screw. A better method is to use optical interference. Remove the plate Q and spindle R' and mount a glass plate, with a worked surface face downwards, in place of them. On the top of pin P put a convex lens of small curvature. Newton's rings can be produced in the usual way between plate and upper lens surfaces. Use sodium light and watch the rings with a microscope.

On working the screw M up or down the pin P rises and the rings grow from or contract into the centre, respectively.

Take readings of the screw head for every ten rings passing one point and calculate at once the unit. The following is a sample table:—

Units on wheel N corresponding to 10 rings.			
Up.	Up.	Down.	Down.
5900	5930	5950	5850
5920	6000	5900	5900
5920	5950	5870	5880
5940	5900	5940	5900
5900	5850	5900	6000
5880	—	5850	—
Mean ...	5920	Mean ...	5890

Thus 590 units correspond to 1 ring = $\lambda/2$.

„ 1 unit „ = 4.9×10^{-8} cm.

The wave-length is a standard unit of the order μ and is 1200 times the unit of the instrument. It would be an advantage to have a standard unit of the order of the instrument, *i.e.*, $\mu\mu$. The greatest and least readings in the above table differ by about 2 per cent. This large error is partly due to inaccuracy in reading the edge of the rings (this might produce 1 per cent. error on 10 rings), but is also due to the fact that the cover is not on the contacts during this calibration, so that thermal expansions occur in them. The cover could be on during calibration, but in the present case it was not considered necessary.

V. Sources of Error: Precautions.

Movements are Normal to Contact Surfaces.—The levers are bent in order that (a) the turning edges of the fulcra, (b) the contact point of each lever on the next, (c) the contact of screw on the first lever, and (d) the contact P and Q where measurements are made, should all lie in one horizontal plane. Thus when the actuating screw works up or down by a small amount there is normal displacement at every contact surface and no scraping of one surface on another. If only these small movements are made we can thus avoid end strain among the levers or actual sliding, which would cause sudden alteration in leverage and jerky working.

Strains in Levers.—The levers conspire to produce minification, each long arm rests on the next short arm and is moved by it. There is no large stress anywhere in the system. The actual pressures (a) between fulcra and blocks, and (b) between lever and lever have alternate maxima and minima from end to end of the system, the greatest differences being at the left end of the system. But the strains are all due to constant gravitation stresses. There seems no reason to expect that in such a set of well-oiled contacts, irregular strains should arise from the mere working of the system, when measurements are made. In actual trial the micrometer is found to work so uniformly that one feels confident that the strains are exceedingly regular, and that each link in the system used does add accuracy as well as sensitiveness.



Longitudinal Displacements.—The levers are allowed three degrees of freedom, a rotation on vertical axis, a translation across the girder and a translation along the girder. In each case the play is very small. It is very desirable that the levers should have freedom without using it.

It is important to have the levers equispaced, for if the small arms have the same length in each lever, a small longitudinal displacement of any lever (except the first and last) will not seriously change the total leverage. Thus suppose the second lever, fig. 1, be moved a small distance to the right, the first lever will gain and the second will lose leverage in the same ratio. But if the movement be continued, the short arms of the two levers being now unequal, the first lever gains leverage in greater ratio than the second loses it. The first and last levers are exceptions. If the first lever move by a small amount to the right it *alone* loses leverage. If the last lever move to the right, the fifth lever *alone* gains leverage. Hence the first and last levers should not be allowed to move longitudinally during an experiment.

If work of high accuracy is being done, it is therefore necessary to frequently set the levers in those exact places for which the instrument has been calibrated. The two other degrees of freedom would produce errors of a smaller order.

The Oil Baths.—These (1) lessen jerk in case the levers slide, and (2) keep the contacts free from dust and from corrosion by contact with the air. It will be seen that of the 13 contact places in the lever system only two are exposed to the air, the first and the last. If particles of dust were allowed to fall on the contact surfaces, they might work into the contact, producing serious error, especially at the left end of the instrument. Dust falls on the oil surface and floats there, the contacts below being thus kept clean.

Vibrations.—Tremors from the ground cannot easily reach the micrometer. There are two possible ways by which they can do so, (1) ascend through the massive cement slabs interleaved with rubber, pass to the top of frame S, then descend the rubber cords S' which are loaded with 28-lb. bars at intervals, or (2) pass along the rubber pulley cord; but this is too light and lax to transmit such tremors as will affect the suspended body, weighing about 80 lbs.

Measurable tremors only reach the micrometer rarely. The above insulating arrangements act so well that ordinary measurements more than $5\ \mu\mu$ can be done throughout the day. Finer work is done at night after 12 o'clock. It may be mentioned that the instrument is set up in a vault, whose floor is 12 feet below ground level, and that a mechanical workshop is immediately overhead.

Thermal Expansions.—Expansion in the direction of the length of the apparatus can be ignored, whereas expansion perpendicular to the levers would introduce large error. The following parts, therefore, should, if possible, be made of invar—cage F', spindle R', pin P, lever pins C, fulcrum B. But these vertical expansions become of decreasing importance as we pass from the cage F' to the right of the apparatus, so that thermal expansion in the screw and last lever pin can be ignored. Suppose the spindle R' is of brass (which must be used in magnetic work) and is 20 cm. long; if its temperature change 1° , the movement is 4×10^{-4} cm., i.e., 10,000 units on the instrument, whereas if the first lever pin is of brass, and 1 cm. long, a change in temperature of 1° would be 5×10^{-9} cm., i.e., $1/10$ unit.

When a new set of measurements is about to be taken, it is always necessary to uncover the micrometer and clean the contacts P, Q. On putting the cover on again, thermal expansion will be seen in "creeping" of the contact. For the most delicate work, 1 hour and sometimes more is required for temperature equilibrium to be established.

Magnetic Strains.—When magnetic work is in hand, *e.g.*, magnetic expansion,* the girder and cage F' and levers, and all bolts and nuts must be of non-magnetic substance.

The Contact Surfaces.—Steel, iron, platinum, copper, carbon, and other surfaces have been tried for P and Q, but iridio-platinum seems best of all, and dry rouge on washleather is used for polishing. High polish is essential for sharp readings. Again, the ordinary use of the surfaces, involving frequent make and break, damages them, say, in one hour of continuous use, and the readings become uncertain.

It has frequently been urged by critics that as the surfaces P, Q approach one another, having a potential difference of, say, 1 volt, there will be a spark between them before the surfaces touch, and that this sparking will be irregular and a source of uncertainty in the finest measurements. This sparking probably always occurs, but it is not irregular within experimental limits, as is shown by the fact that the readings of the instrument are consistent.

As regards the length of this spark-gap, the present writer has made investigations for low voltages, from 100 volts to 0.2 volt,† and has found that for P.D. 1 volt the gap is 10 $\mu\mu$, and that the relation between gap and P.D. is linear. Assuming a combination of the linear relation, and taking the P.D. used in the micrometer work, 1/100 volt, the gap would be about 1/10 $\mu\mu$. So that, whether regular to 20 per cent. or not, the sparking would introduce no measureable error.

VI. *Applicability.*—The method has been shown to be applicable to various measurements:—

(1) Telephone diaphragm movements and hence the amplitude of the least audible sound.‡

(2) The expansion of iron, steel, nickel, and of non-magnetic bodies when subject to changes of magnetic field.§

(3) As a coherer. The two contact points can be brought to molecular distance apart without touching; they then constitute a very sensitive and adjustable coherer.||

(4) The distance of discharge of two surfaces maintained at a different electric potential.¶

There are other obvious applications, *e.g.*, (a) thermal expansibility;

* See 'Roy. Soc. Proc.,' 1903.

† See 'Roy. Soc. Proc.,' 1904.

‡ See 'Phil. Mag.,' 1900, and ensuing paper.

§ See 'Electrician,' 1901 and 1902, and 'Roy. Soc. Proc.,' 1903.

|| See 'Phil. Mag.,' March, 1901.

¶ See 'Roy. Soc. Proc.,' 1904.

(b) the Newtonian constant, by the measurement of the movements of a pendulum from the vertical under the attraction of a large mass.

VII. *Comparison with other Micrometers.*—Other instruments capable of fine measurements are :—

(a) *The Optical Lever*, on the Gauss-Poggendorff principle. The movement to be measured causes rotation of a mirror, so that a spot of light from it traverses a scale. In some cases levers are used to magnify the effect.* The form used by Nagaoka† is very sensitive: there is no lever, but the movement of the spot is examined by a microscope. The smallest recorded reading in this way is 2.3×10^{-7} cm.

(b) *Interference Methods.*—The Fizeau method has been developed by Abbé, Pulfrich, and Tutton. The distance between the interfering surfaces is small.

The interferimeter, where the interfering surfaces are far apart, has been developed by Michelson into an accurate and adaptable instrument. The unit in these methods is about 10×10^{-6} cm. The objection to these methods is that the interference bands are so far from sharp that it is difficult to locate accurately the centres of two consecutive bands, and to divide the intervening space into any number of equal parts.‡

(c) *The Microscope.*—This is still less sensitive than interference methods, the smallest possible reading being 2×10^{-5} cm.

To enumerate the qualities desirable in a micrometer :—

(i) *Practical Sensitiveness* (i.e., the smallest distance which can be accurately read)—

The electric micrometer ...	4×10^{-8} cm.
optical lever	2.3×10^{-7} „
interference methods ...	1×10^{-6} „
microscope	2×10^{-5} „

(ii) *Range.*—The electric micrometer can read quite 10,000 units $= 4 \times 10^{-4}$ cm.

In the other micrometers there is a field of view which determines the range. Or, if a micrometer screw be used to restore zero reading, the practical sensitiveness is that of a *working* screw, which is not great.

(iii) *Quickness of Action.*—The optical lever, interference methods, and

* See Shelford Bidwell, 'Phil. Trans.,' A, 1888.

† See 'Phil. Mag.,' 1894.

‡ Recently, a modification of Michelson's method has been made by C. W. Chamberlain (see Kinsley, 'Phil. Mag.,' May, 1905), by which the sensitiveness is greatly increased, and movements of 3×10^{-7} cm. have been measured.

microscope, are quick within the range of the field of view, outside that range they are at least as slow as—

The electric micrometer, in which time must be taken for the movable contact to bridge over the gap to the fixed contact.

(iv) *Calibration.*—The interference methods here have an advantage over other micrometers in that no calibration is necessary, the wave-length being a standard known length.

The electric micrometer and the microscope can be readily calibrated, the former by interference bands, and the latter by a line standard bar.

The optical lever cannot be calibrated with accuracy; any method takes account directly or indirectly of the effective length of the lever. This length is small and difficult to measure with precision.

(v) *Freedom.*—In the interference methods and microscope the measuring apparatus does not press on the moving body, so this need not be rigid. This is an advantage.

In the optical lever and electric micrometer, actual mechanical pressure, though not necessarily large, is essential. If perfect freedom of the moving body is required, these methods are inadmissible.

(vi) *Compactness.*—The optical lever is the most simple and compact micrometer, and the electric micrometer is the least so, in the form described above. But the latter instrument could, if desirable, be reduced to quite a small size, without detriment to its usefulness.

I am glad to acknowledge my indebtedness to the Royal Society for two grants in aid of these researches, and to Professor W. H. Heaton for his unfailing encouragement and general furtherance of the work.

The Amplitude of the Minimum Audible Impulsive Sound.

By P. E. SHAW, B.A., D.Sc.

(Communicated by Professor J. H. Poynting, F.R.S. Received March 30,—
Read April 13, 1905.)

I. *Introduction.*—Investigations of amplitude for *continuous sounds* produced in a telephone by alternating current have been made by Lord Rayleigh,* Franke,† Cross and Mansfield.‡ Lord Rayleigh found by an indirect process the value $0.05\ \mu\mu$ for frequency 512, and $0.7\ \mu\mu$ for frequency 256. Other values found by Lord Rayleigh§ are: $0.8\ \mu\mu$; $1.27\ \mu\mu$. Toepler and Boltzmann obtained results of the same order. These results cannot be tabulated as the conditions are different, and in some cases unknown. Franke, by more direct measurement, obtained a value $1.2\ \mu\mu$.

The present writer|| found by direct measurement a value $0.4\ \mu\mu$ in the case of an *impulsive sound*.

In each of these researches the micrometer was not sensitive enough to actually measure the least-audible amplitude; the relation of current to amplitude was determined for relatively large amplitudes, and separate measurements were made of the current which gives the least audible sound. Extrapolation then gave the amplitude in question.

The present writer measured as little as $2.1\ \mu\mu$, so that he was less likely to err in using extrapolation than Franke, whose smallest observed amplitude was $52\ \mu\mu$.

The present paper shows how the amplitude of the smallest audible sound can be measured directly without extrapolation; it is even possible, as the tables show, to measure movements whose amplitude is too small to be audible.

With the instrument described in the previous paper,¶ movements as small as $0.4\ \mu\mu$ can be observed; the minimum audible has been again investigated on the same lines as before.

The value obtained for a sensitive ear is $0.7\ \mu\mu$, as shown below. It refers to a telephone of usual construction whose diaphragm fundamental is about 580, the sound being perceived by the right ear of the writer, expecting the sound.

* 'Phil. Mag.,' 1894, vol. 37.

† 'Proc. Tel. Eng.,' vol. 16.

‡ 'Proc. Amer. Acad.,' vol. 20.

§ See Rayleigh's 'Sound,' 2nd edit.

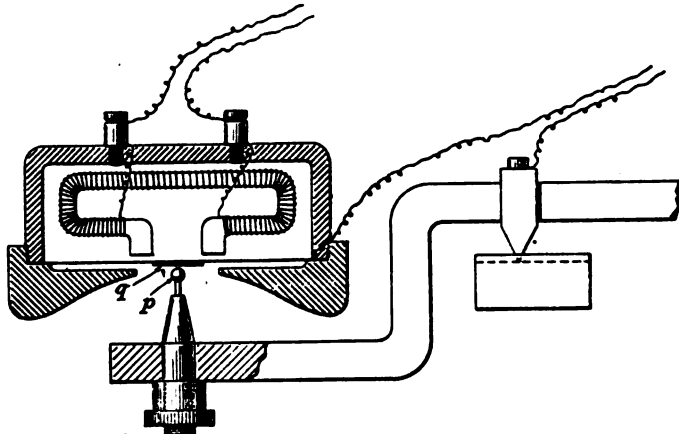
|| "Electric Micrometer," 'Phil. Mag.,' 1900.

¶ "Improved Electric Micrometer," p. 350, *supra*.

II. *Method.*—There are two distinct parts in the determination :—

A. Observe the position of the diaphragm q (see fig. 1) at rest by making contact pq , draw away p by working the lever system, and pass a steady current through the telephone, so as to move the diaphragm to a new position of rest.

FIG. 1.



Now move up p slowly towards the diaphragm, watching the micrometer screw (fig. 1, last paper), and listening for contact. Thus measure the movements due to a set of steady currents down to such small ones as cause imperceptible motion. Plot the relation between movement and current.

B. Apply the ear to the telephone and pass through the same set of currents as in Section A. For each current, except the smallest ones, a sound is heard when the key is released. We thus learn the relation of current to audibility; the curve in Section A gives at once the relation of amplitude to audibility.

The sound is impulsive, for the diaphragm is released from a position of strain, vibrates under considerable damping, and soon comes to rest.

Both right and left ear were used. Speaking generally, both ears would be considered to be normal, but as the writer has had great practice in listening to faint telephone sounds with the right ear, probably that is abnormally acute.

The research was conducted in a vault below ground between 12 o'clock and 4 o'clock at night, so that extremely quiet conditions prevailed.

III.—*Amplitude Tables* :—

C = current in terms of 1 micro-ampère as unit.

M = micrometer reading.

$\mu\mu$ = " " rendered in terms of 10^{-6} mm.

I.—Old Receiver.

C.	Set 1.			Set 2.		
	M.	$\mu\mu$.	Remarks.	M.	$\mu\mu$.	Remarks.
3	—	—	Inaud. Right Inaud. Left	—	—	Inaud. Right Inaud. Left
4	—	—	Just aud. Right Inaud. Left	1, 2, 1	0.6	Just aud. Right Very faint. Left
7.8	2, 3, 2	1.1	Aud. Right Just aud. Left			Aud. Right Just aud. Left
9	3, 2½, 3	1.4	Aud. Right Aud. Left			Aud. Right Aud. Left
10	4, 4, 3	1.9	" "			" "
13	5, 6, 5	2.3	" "	6, 5, 6	2.4	" "
20	6, 7, 6	2.8	" "	7, 8, 7	3.1	" "
40	10, 10, 10	4.7	" "			

II.—Old Receiver.

C.	Set 1.			Set 2.		
	M.	$\mu\mu$.	Remarks.	M.	$\mu\mu$.	Remarks.
2	—	—	Inaud. Right Inaud. Left	1, 1½, 1	0.5	Inaud. Right Inaud. Left
3	—	—	Just aud. Right Inaud. Left	2, 1½, 1½	0.7	Just aud. Right Inaud. Left
4	—	—	Aud. Right Just aud. Left	2, 2, 2	1.0	Aud. Right Aud. Left
7.8	3, 3, 3	1.4	" "	3, 3, 2½	1.4	" "
9	3, 4, 4	1.8	" "	4, 4, 3	1.8	" "
10	4, 4, 4	1.9	" "	5, 4, 4	1.9	" "
13	5, 5, 6	2.5	" "	6, 5, 6	2.6	" "
20	6, 7, 7	3.1	" "	7, 7, 6	3.1	" "
40	8, 8, 8	3.7	" "	8, 8, 8	3.7	" "

III.—New Receiver.

C.	Set 1.			Set 2.		
	M.	$\mu\mu$.	Remarks.	M.	$\mu\mu$.	Remarks.
2	1, 1, 1	0.47	Inaud. Right Inaud. Left	1½, 1, 1	0.5	Inaud. Right Inaud. Left
3	1½, 1½, 1½	0.7	Inaud. Right Inaud. Left	2, 1½, 2	0.8	Just aud. Right Inaud. Left
4	3, 3, 3	1.4	Aud. Right Aud. Left	3, 3, 3	1.4	Aud. Right Aud. Left
7.8	4, 3, 4	1.7	" "	3, 4, 4	1.7	" "
9	5, 5, 5	2.3	" "	5, 5, 5	2.3	" "
12	7, 8, 8	3.8	" "	8, 7, 7	3.7	" "
17	10, 12, 12	5.0	" "	10, 11, 11	4.8	" "
40	24, 25, 25	12	" "			

IV.—New Receiver.

C.	Set 1.			Set 2.		
	M.	$\mu\mu$.	Remarks.	M.	$\mu\mu$.	Remarks.
1·5	1, 1 or less,	0·4	Inaud. Right			
	1 or less		Inaud. Left			
2·5	2, 2, 1½	0·9	Just aud. Right			
			Inaud. Left			
3	3, 3, 2½	1·4	Aud. Right			
			Aud. Left			
3·5	4, 4, 4	1·9	" "	—	—	Inaud. Right
						Inaud. Left
4	5, 5, 4½	2·3	" "	1, 1,	0·4	Inaud. Right
				1 or less		Inaud. Left
7·8	7, 7, 7	3·3	" "	2, 1, 1	0·7	Aud. Right
						Aud. Left
10	8, 8½, 9	4·0	" "	2, 2, 2	0·9	" "

In Set 2 above another ring was placed under the diaphragm to raise it to a greater distance from the magnet poles, and so render the receiver less sensitive.

The Curves I and II refer to one instrument.

" III „ IV „ another instrument.

Curve IV₂ is for the second instrument rendered less sensitive.

The curves are not simple in form, which may be partly due to errors in measurement, as we are near the limit of the instrument. But, as in the former paper,* it is obvious that, according to the exact tightening of the diaphragm, we obtain a different characteristic curve for it. Thus III and IV are for the same instrument, but no doubt the clamping conditions are different in the two cases.

IV. *Results*.—In the curves the cross lines show where the sound is just audible for the right ear, the circles where it is just audible for the left ear.

Averaging the results, we obtain 0·7 $\mu\mu$ for the right ear and 0·9 $\mu\mu$ for the left.

On reference to the first section of this paper, it will be seen that the above result for impulsive sound is in close agreement with those obtained by Rayleigh, Boltzmann, and others for continuous sound.

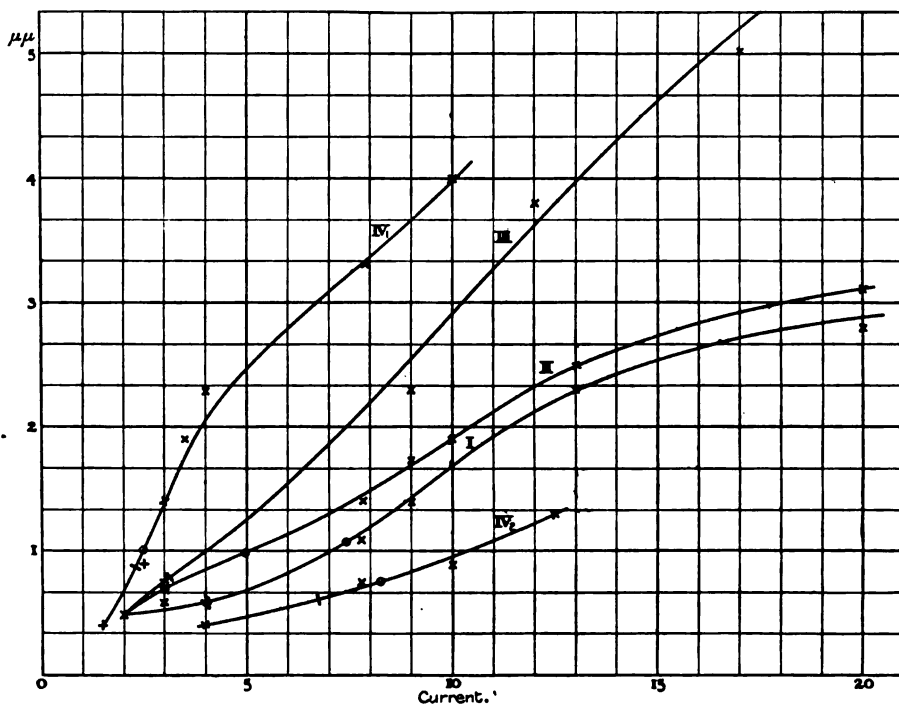
The fundamental of the diaphragm when clamped hard to the case was found, by testing it against tuning-forks, to have frequency about 580. Throughout the amplitude measurements care is taken to clamp the diaphragm firmly, so as to insure that its movements are purely flexural.

In the former paper† a scale of loudness was drawn up. It now stands amended in column A.

* *Loc. cit.*

† *Loc. cit.*

FIG. 2.



	A.	B.
Just audible	0.7 $\mu\mu$	0.14 $\mu\mu$
„ comfortably loud	50	10
„ uncomfortably loud ...	1000	200
„ overpowering	5000	1000

The word “just” here implies, in each case, the lower limit.

The amplitude of the diaphragm must not be confused with that of the air which it vibrates. Lord Rayleigh* obtains a relation between these two amplitudes by considering the space between diaphragm and tympanum of the ear to be an air-tight cylinder, the diaphragm acting as a piston moving at one end. Roughly speaking, the ratio of the two amplitudes is 5:1. Using this factor, we obtain column B for air amplitudes under the conditions of the above experiments.

Though 0.14 $\mu\mu$ is the smallest audible amplitude in air to an expectant ear when the conditions as to silence are exceptionally favourable, yet 10 $\mu\mu$ is the amplitude for the smallest audible sound in air about which the ear can be quite sure when the conditions are normally favourable and the ear not listening for the sound.

* *Loc. cit.*

This number is used in the next section.

V. *Large Sound Amplitudes.*—It is difficult, or even impossible, to measure the air amplitude near the source of a great impulsive sound—*e.g.*, an explosion, but indirectly we can obtain some idea of this large amplitude by observing the distance at which the sound is distinctly just audible, and applying the law of sound radiation.

If the radiation be *cylindrical*, $i \propto a^2$, or

$$a_1^2 r_1 = a_2^2 r_2 \quad (\text{I})$$

where i = intensity, a_1, a_2 amplitudes at distance r_1, r_2 from the source.

This would occur if the source were a long line or if the radiation took place between near parallel walls.

If, however, the radiation be *spherical*, and the source be one of simple expansion and contraction around a centre, $i \propto a^2$, or

$$a_1 r_1 = a_2 r_2 \quad (\text{II})$$

This occurs in an atmosphere of uniform temperature and free from distinct strata. But in reality there are (1) reflections upwards produced from the earth, (2) reflections downwards from damp layers in the upper air, (3) total reflections from upper or lower layers of higher temperature, and therefore higher sound velocity, (4) deflections due to air-currents.

The spherical law will give us a basis for rough calculations, but the many anomalies in sound transmission are due to these deflections, and not to any truly cylindrical radiation.

One or two examples, in which we know data, are given:—

Thunder.—This has a vertical line-source, but for a *distant* observer it becomes a point-source. If 10 miles be the maximum distance at which it can be heard, expression II gives, taking $r_1 = 2$ yards,

$$a_1 = 1/12 \text{ mm.}$$

This value for r_1 might be possible. It should be observed that a_1 is *at most* 1/12 mm., probably much less, for *near* a line-source cylindrical radiation would occur.

Cannon-Firing.—This is an instance of a simple point-source. If 30 miles be taken to be a maximum distance for the sound to carry, the amplitude at a place two yards to the side of the muzzle of the gun where the nearest gunner stands would be about 1/4 mm. This seems to be the largest sound amplitude of which we have any knowledge.

The case recorded in 'Knowledge,' June, 1901, in which firing was heard at 140 miles from the source, is peculiar. Some deflections must have

occurred, for over a wide zone of from 10 to 50 miles from the source no sound was heard.

Volcanic Eruptions.—The sound commences not at a point, but over a large horizontal area. Suppose the greatest distance to which sound carries is 500 miles, the amplitude at one mile from the source would be $1/200$ mm.

In the great eruption of Krakatoa, sounds were heard 5000 miles away. If the sound really travelled through air (and not through the earth), it must have had a succession of reflections to take it round nearly one earth-quadrant.

In making these estimates of large amplitudes (which are intended to show merely the order) the spherical law is considered to hold good while amplitude varies from $10\ \mu\mu$ to $100,000\ \mu\mu$ or more. This is not strictly true; but the errors caused by deflections in the atmosphere are uncertain *plus* and *minus* quantities, at least as large as those involved in taking the spherical law to hold throughout, so that it would be practically useless to attempt a more accurate calculation.

I am glad to acknowledge my indebtedness to the Royal Society for two grants of money whereby I have been able to develop these researches.

*Note on Dr. H. A. Wilson's Memoir "On the Electric Effect of Rotating a Dielectric in a Magnetic Field."**

By S. J. BARNETT, Palo Alto, California; U.S.A.

(Communicated by Professor Larmor, Sec. R.S. Received February 6,—
Read June 8, 1905.)

While Dr. Wilson's experiments undoubtedly confirm the electron theory of Lorentz, as do the earlier experiments of Blondlot† on the motion of air through a magnetic field, to which Dr. Wilson does not refer, he has seriously misinterpreted this theory in stating that, according to it, the electromotive force induced in an insulator with dielectric constant K moving in a magnetic field bears the ratio $(K-1)/K$ to the electromotive force induced in a moving conductor. As a matter of fact, it is not the induced intensity or electromotive force which differs from substance to substance, and which differs according to different theories, but the displacement or charge produced by this intensity or electromotive force.

The calculation of the intensity or electromotive force induced in matter by its motion in a magnetic field, the "motional" intensity or electromotive force of Mr. Heaviside, is very simple on the theory of Lorentz. Thus, if an electron with charge q , a constituent of any kind of atom whatever, moves with velocity v in a magnetic field in which the induction is B , it will, in accordance with the law of Ampère applied to the convection current, be acted upon by a force

$$F = qVvB.$$

The force per unit charge upon the electron, or the motional intensity in the moving substance, is thus

$$e = F/q = VvB,$$

and is wholly independent of the nature of the moving substance. Hence the induced or motional electromotive force, E , which is the line integral of the motional intensity e , is likewise independent of the nature of the moving substance.

Thus, instead of Dr. Wilson's equation,

$$E = n\pi(r_2^2 - r_1^2)H(K-1)/K,$$

we have

$$E = n\pi(r_2^2 - r_1^2)H,$$

H , the intensity of the magnetic field, being written for B , to which it is equal in magnitude.

* 'Phil. Trans.,' A, vol. 204, p. 121.

† 'Journal de Physique,' vol. 1, p. 8, 1902.

Hence, in place of Dr. Wilson's equation,

$$E = V(C+C')/C,$$

we have

$$E = V(C+C')/C \cdot K/(K-1) \quad \text{or} \quad V = E(K-1)/K \cdot C/(C+C'),$$

the result which is confirmed by Dr. Wilson's experiments, our $E(K-1)/K$ being equal to his E .*

When Dr. Wilson's abstract† appeared in America last July, I noticed at once the need for the above correction, but refrained from making it until the appearance of his complete memoir, hoping there to find the derivation of his curious result. The memoir, however, gives no derivation of the erroneous statement.

It may be of interest to state that in 1902 I started to construct apparatus for an investigation of this subject by a method different from Dr. Wilson's.

* To avoid ambiguity, let us write

$$\left(\frac{K-1}{K}\right) n\pi H(r_2^2 - r_1^2) = E,$$

the motional E.M.F. according to Dr. Wilson's theory, and

$$n\pi H(r_2^2 - r_1^2) = E_2,$$

the motional E.M.F. according to Lorentz. From these equations we get the relation

$$E = E_2 \left(\frac{K-1}{K}\right).$$

Dr. Wilson's second equation on p. 123 of his memoir then becomes

$$-\frac{2Q}{K} \log \frac{r_2}{r_1} = -(V_2 - V_1) + E \quad (\text{Wilson}),$$

$$\text{or} \quad -\frac{2Q}{K} \log \frac{r_2}{r_1} = -(V_2 - V_1) + E_2 \left(\frac{K-1}{K}\right) \quad (\text{Lorentz}).$$

Making the transformations indicated by Wilson, we get

$$-\frac{Q}{C} = -V + E \quad (\text{Wilson}),$$

$$\text{or} \quad -\frac{Q}{C} = -V + E_2 \left(\frac{K-1}{K}\right) \quad (\text{Lorentz}).$$

$$\text{And finally} \quad V(C+C') = CE \quad (\text{Wilson}),$$

$$\text{or} \quad V(C+C') = CE_2 \left(\frac{K-1}{K}\right) \quad (\text{Lorentz}).$$

Now Wilson's experiments proved

$$\frac{V(C+C')}{C} \text{ equal to } E,$$

which is the same thing as proving

$$V \left(\frac{C+C'}{C}\right) \text{ equal to } E_2 \left(\frac{K-1}{K}\right).$$

But E_2 , not E , is the motional E.M.F. Thus the experiments proved V , or Q ($= -\frac{CC'}{C+C'} \cdot E_2 \left(\frac{K-1}{K}\right)$), to be proportional to the E.M.F. in any theory and to $\frac{K-1}{K}$.

† 'Roy. Soc. Proc.' June 2, 1904.

Lack of funds, however, put an early end to the work, and it has been resumed only lately with the aid of a grant from the Carnegie Institution.

Note on the Preceding Paper. By Professor LARMOR, F.R.S.

This paper is communicated by request of Dr. Barnett. The footnote inserted on p. 368 was received on March 23 in reply to a request for further information as to his meaning.

It would seem that objection is taken to Dr. Wilson's use of the somewhat ambiguous term electromotive force. It does not appear that Dr. Wilson's experimental result is disputed, nor is any other theoretical deduction offered in place of his one.

The proposition proved by Dr. Wilson is that rotation of a cylindrical condenser around its axis, in a longitudinal magnetic field, produces the same electromotive effect as if the condenser were at rest, and a potential difference equal to $(1 - K^{-1})U$ were impressed between its coatings, *e.g.*, by connecting them through a battery of that electromotive force. In this expression U is the Faraday potential-difference that would be excited between the coatings of the rotating condenser if they were connected by a conducting wire that moved along with them. Dr. Barnett apparently wishes to omit this factor $1 - K^{-1}$, and to rectify this omission by making the charge equal to the difference of potential multiplied by the capacity multiplied by $1 - K^{-1}$.

If the moving dielectric were air, as in the experiment quoted from Blondlot by Dr. Barnett, the influence of the factor $1 - K^{-1}$ of course could not be detected; the result must then in fact practically be the same, on any theory, as if the dielectric were vacuum.

Colours in Metal Glasses, in Metallic Films and in Metallic Solutions.—II.

By J. C. MAXWELL GARNETT.

(Communicated by Professor J. Larmor, Sec.R.S. Received May 15,—Read June 8, 1905.)

(Abstract.)

In the first section of this paper it is pointed out that one and the same metal may cause a great variety of different colours, just as the colour of gold vapour differs from the colour of the light reflected from gold as well as from the colour of the light transmitted by gold leaf. While the ultimate cause of the colour of a metalliferous medium is to be found in the structure of the metal molecule itself, the arrangement of these molecules, according to any fixed law, causes them to affect one another's free periods in a definite manner, and thus gives rise to corresponding optical properties. The object of this paper is to discover, by means of these optical properties, the molecular arrangement (microstructure) of various metal glasses, of colloidal solutions of metal and of metallic films.

Expressions giving the refractive index and the absorption coefficient (the optical constants) of a compound medium consisting of metal (1) in small spheres (granular), and (2) in discrete molecules (amorphous), diffused through an isotropic non-dispersive transparent medium (the solvent), are next investigated in terms of the corresponding optical constants of the normal metal.

The particular formulæ which apply when the volume proportion of metal in the compound medium is small, as in the case of metal glasses and of "colloidal solutions" of metal in water, are also obtained, and it is found that while spheres of any metal, so diffused that there are many to a wave-length of light, will produce colours which vary with the refractive index of the solvent, diffused molecules of any metal produce, by transmitted light, a colour (the vapour colour) which is independent of that refractive index.

By means of these formulæ and of the optical constants of gold, silver, and copper, experimentally determined for monochromatic light of several different wave-lengths, the numerical values of the corresponding optical constant which would be possessed by diffusions of spheres and of molecules in glass, water, or vacuum, are calculated and tabulated. Defining the absorption of light of wave-length λ by any absorbing medium as being

the logarithm of the ratio of the intensities of that light before and after traversing a unit-length of the medium, graphs are given of the calculated absorptions of these diffusions. Curves are also shown representing the absorptions of specimens of gold ruby glass, of silver stained glass, and of copper ruby glass, as measured at the National Physical Laboratory.

A comparison of these curves with the graphs for gold spheres and for gold molecules in glass, and a collation of the results with others already obtained in a previous communication,* leads to the conclusion that the colour of gold ruby glass is due primarily to the presence of small spheres of gold. The irregular blue and purple colours sometimes exhibited by gold glass are then explained by the presence of crystallites caused by the coagulation of the gold spheres. Again, when the corresponding graphs with water as solvent are compared with the absorptions of colloidal gold as measured by Ehrenhaft,† little doubt remains but that colloidal gold consists of small spheres in suspension; the blue colour produced by particles coarser than the small spheres is, as in the case of glass, due to the red light being reflected by the crystallites and so not transmitted.

The close similarity between the observed absorptions of yellow glass stained with silver, and the calculated absorptions of a diffusion of silver spheres in glass—the calculated absorptions of a diffusion of silver molecules in glass are quite different—indicates that the stained region must contain small spheres of silver. Ehrenhaft's‡ description of the nature and position of the absorption band observed in the spectrum of colloidal solutions of silver, describes so well the position of the absorption band determined by calculation for a diffusion of silver spheres (but not of silver molecules) in water, as to justify the conclusion that the bulk of the silver present in colloidal solution is in the form of small spheres: little, if any, being in true solution (*i.e.*, molecularly subdivided); and this conclusion is confirmed by the fact that the refractive index of a colloidal solution of silver, which was measured by Barus and Schneider,§ is precisely that which calculation shows to be possessed by a diffusion of silver spheres (but not of molecules) in water.

Measurements, made by Sir William Abney, of the intensities with which light of various wave-lengths is reflected from the interface between the stained and unstained regions of one of the specimens of silver glass which had belonged to Stokes, when held with the stain turned away from

* 'Phil. Trans.,' A, 1904, pp. 385 to 420.

† Felix Ehrenhaft, 'Ann. der Phys.,' vol. 11, p. 489 (1903).

‡ *Loc. cit.*, p. 507.

§ Barus and Schneider, 'Zeitschr. f. Phys. Chem.,' vol. 8, p. 278.

the source of light, are in general accordance with the reflective powers calculated on the hypothesis that small spheres of silver are distributed throughout the stained regions, the maxima corresponding to light of wavelength about $\lambda = 0.436$ in both cases. If the silver in the glass had been molecularly subdivided the maximum would have been at about $\lambda = 0.360$. The presence of silver spheres (but not of discrete molecules of silver) throughout the stained region thus accounts for the blue reflection, in accordance with Stokes,* as well as for the amber colour of silver glass viewed by transmitted light, proving that both colours were due to suspended particles of silver.

A comparison of the observed absorptions of copper ruby glass with the calculated absorptions of copper spheres and of copper molecules diffused in glass, shows that copper ruby glass owes its colour to the presence in the glass of small spheres of metallic copper,† while some copper molecules are probably also present. Although it has thus been proved that gold and copper ruby glasses and silver glass owe their colours to diffused spheres of the metal, the metals which colour some other glasses cannot be present in the metallic form; for example, the deep blue colour of cobalt glass cannot be due to diffused metallic cobalt, which, according to calculation, would give a reddish colour by transmitted light akin to that observed by Ehrenhaft‡ in a "colloidal solution" of that metal.

The colours produced in gold, silver, and soda glasses by the radiation from the emanation from radium, give rise to the suggestion that all glasses contain free ions of metal, and it is by the discharge of these ions and the consequent reduction of the metal (so that the metal is diffused in the glass), that cathode and Becquerel rays are able to colour the glasses.

Expressions are obtained giving the absorptions and reflective powers of amorphous or granular forms of gold and silver, the specific gravity of which is any proper fraction, μ , of that of the metal in its normal state. Curves are constructed to show how the values of these expressions, and thus also the colours exhibited by transmitted and by reflected light, vary with μ .

A comparison of these calculated colour changes with those actually shown by gold and silver films, such as those deposited on glass by Faraday,§ and

* Stokes, "On the Change of Refrangibility of Light," 'Phil. Trans.,' 1852; 'Collected Papers,' vol. 3, p. 316.

† Stokes (*loc. cit.*, vol. 4, p. 245) thought copper ruby glass was coloured by suboxide of copper, and attributed the change of colour in some specimens to suspended particles of the metal.

‡ Ehrenhaft, *loc. cit.*, p. 506.

§ Faraday, Bakerian Lecture, 'Phil. Trans.,' 1857.

by Beilby,* when subjected to heat and to pressure, indicates that (a) the films as first prepared are in the amorphous or granular phase, and (b) heating diminishes the density of the film, while pressure is able to increase that density again, and finally, (c) this diminution of density is probably effected by the passage of metal from the amorphous to the granular phase, and by the growth of the larger granules at the expense of the smaller, while increase of density is accomplished by changing some of the metal from the granular to the amorphous phase.

The optical properties of Carey Lea's† so-called solutions of allotropic silver show that they consist of small spheres of silver in suspension in water. From this and other evidence it is shown that the suggestions made in the former paper‡ that Carey Lea's silver was not allotropic, but consisted of normal silver in a finely divided (but not necessarily granular) state, was almost certainly correct.

The three forms of silver discovered so long ago as 1861 by Hermann Vogel,§ were probably the amorphous, granular, and crystalline forms discussed in this paper.

The paper concludes with the suggestion that many forms of metals which have hitherto been considered to be allotropic, because possessing optical properties distinct from those belonging to the metal in its normal state, are merely cases of fine division. Thus the properties of Bolley's lead,|| of Schützenberger's¶ silver and copper, and of other alleged cases of allotropy cited by Roberts-Austen,** do not require the postulation of an allotropic molecule for their explanation.

* G. T. Beilby, Hurter Memorial Lecture, Glasgow, 1897.

† Carey Lea, 'Amer. Jour. of Science' (1889), and 'Phil. Mag.' (1891).

‡ *Loc. cit.*, p. 419.

§ Hermann Vogel, 'Pogg. Ann.', vol. 117, p. 316 (1861).

|| Cf. Roberts-Austen, 'Metallurgy,' p. 90.

¶ Schützenberger, 'Bull. Soc. Chim.', vol. 30, p. 3 (1878).

** Roberts-Austen, *loc. cit.*

The Evolution of the Spectrum of a Star during its Growth from a Nebula.

By W. E. WILSON, D.Sc., F.R.S.

(Received June 5,—Read June 8, 1905.)

In considering the probable evolution of the spectrum of a star in its different stages from a nebula,* let us first consider a mass of gas at a sufficiently high temperature to be able to radiate waves of light into the surrounding space. If this mass of gas were sufficiently rare to be transparent to all wave-lengths of light except those which it is itself able to radiate, its spectrum would be a bright-line one.†

Sir William Huggins was the first to show, in 1864, that many nebulae gave a simple spectrum of a few bright lines. These lines show the presence of hydrogen and helium. Some other faint lines are also seen, but their origin is at present not known.

As our supposed mass of gas, spherical for simplicity, slowly cools, its density must increase at the centre, and as the density became sufficiently great for the gas to become nearly opaque for light of all wave-lengths, the bright lines of the spectrum, which at first were thin and faint, would continually thicken and finally become a continuous spectrum. When the nucleus had become dense enough to be quite opaque, if no scattering of the light coming from the deepest parts of the nucleus is in operation, the mass would radiate as freely as a "black body," and the spectrum would be an absolutely continuous one. The late Professor G. F. FitzGerald suggested

* [Note, June 8, 1905.—On sending this paper to Professor Larmor for reading at the Royal Society, my attention was again directed by him to the very complete discussion of some of the subjects treated in it that is contained in Sir W. and Lady Huggins' 'Atlas of Representative Spectra,' published by Wesley and Son, 1899. I am glad to be able to refer to this high authority in support of the views herein expressed. Thus it is concluded there that hydrogen, and especially helium, are not confined to any one class of stars, but are common to all stars and nebulae. The influence of partial pressure of the gas, of convection currents, of pressure due to increasing force of gravity, of increase of temperature as well as fall, are also traced, with a general conclusion (p. 75) that "principal types of star spectra should not be interpreted as produced by great original differences of chemical constitution, but rather as successive stages of an evolutionary progress bringing about such altered conditions of density, temperature, and mingling of the stellar gases as are sufficient presumably to account for the spectral differences observed." See also British Association Presidential Address, 1891.]

† Schuster, 'Astro-physical Journal,' January, 1905.

in 1896* that in such a mass of heated gas there would be powerful convection currents, and that these would be able to scatter, and deflect back into the interior, rays coming from the lower depths of the gaseous mass, so that such a mass of heated gas, however thick, could never reach the stage of radiating as a "black body." In fact it would emit the same spectrum as the mass gave before it was dense enough to be quite opaque. If the nebula consisted originally of an enormous mass of extremely attenuated hydrogen, and mixed with it minute proportions of the vapours of other elements such as iron, magnesium, etc., the spectrum of these other elements would not become visible until, in the lapse of time, the elements of high atomic weight gradually gravitated to the centre of the mass, so as to arrive at a density great enough to give rise to the emission of their bright-line spectra. In this gradual process of concentration of the heavier elements to the centre, they would displace the hydrogen, helium, and other elements which have small atomic weight. The heavier elements would in time become the source, in the nucleus of the nebula, of the bright, banded, and almost continuous spectrum; while the lighter and now cooler elements like hydrogen and carbon would begin to give a dark-line spectrum, as Schuster shows, superposed on that from the nucleus, when the temperature gradient became sufficiently steep. This type of spectrum would hold until the star cooled down below the point at which the vapour of the carbon present congealed into droplets of solid carbon, forming a cloud-layer or photosphere in the star's atmosphere.

When this critical temperature was reached, the star's spectrum would evidently undergo a profound change. The cloud layer, if deep enough to be opaque, would entirely cut off the bright-banded spectrum coming from the nucleus, and in its place give us an absolutely continuous one,

* Wilson and FitzGerald, 'Roy. Soc. Proc.,' vol. 60. We were engaged in measuring, by means of a Boys' radio-micrometer, the radiation coming from the positive carbon in an electric arc-light while surrounded with different gases under high pressure.

The arc was enclosed in a strong iron box, on one side of which was attached a steel tube which was closed at its furthest end by a strong lens of quartz. This lens formed an image of the arc on the radio-micrometer.

We found that by suddenly reducing the pressure of the gas in the box, there were convection currents set up in the steel tube, which were able to scatter the light coming from the arc so that the carbon suddenly seemed to become only red hot, and even in some instances the incandescent carbon became quite invisible for some seconds. But for the fact that the ammeter showed us that the current was flowing steadily, we would have assumed that the arc had been quenched.

FitzGerald immediately made the suggestion that we had here an explanation of the cause of the darkness of sun-spots.

Also Schuster ('Astro-physical Journal,' 1905) shows mathematically that this result would be produced by molecular scattering of light, or scattering by suspended particles.

on which would be superposed the dark-line Fraunhofer spectrum as we see in the sun.

In a sun-spot we get a glimpse of the solar spectrum like what it was while the sun was so hot as to prevent the condensation of the carbon clouds. Dr. Johnstone Stoney* was the first to point out this view of the nature of the solar photosphere. He suggested that in the true surface of the photosphere we have a region where the carbon clouds are absolutely raining. The droplets of solid carbon thus fall to a lower level, where the temperature is high enough to re-vaporise them again. A sun-spot seems to be due to an up-rush of hot gases with a temperature high enough to vaporise the clouds, so that we are able to see down into the gaseous nucleus below. The penumbra of a sun-spot may be a region where the carbon rain has ceased and where the clouds are of the nature of cirrus or fog.

The ordinary Fraunhofer spectrum would then be due only to the vapours of such elements as from their atomic weight would lie above the carbon clouds, in addition to such vapours as get carried up by the powerful convection currents which must exist on account of the rapid temperature gradients caused by the great radiation from the clouds. The spectrum of a sun-spot is just what we should expect if the radiation is coming from a gaseous layer hotter than the clouds; for it consists of bright bands and lines, crossed by the absorption lines of the vapours which lie between the cloud layer and the deep-seated part of the inner gaseous nucleus.

When we increase the depth or the partial pressure of a vapour giving an absorption spectrum we get more and more dark lines, and also a widening of them into bands, until ultimately when the depth is sufficient to become opaque, the spectrum, as has been previously shown, must assume the character of a continuous one.

Sir William Huggins has shown that by reducing the partial pressure of calcium vapour, the numerous lines in the spectrum of this body gradually disappear, leaving H and K only. And Liveing and Dewar record an observation showing that it is even possible to wipe out the K line, when the remaining spectrum consists of only the one line H.

If, instead, the absorption spectrum of calcium vapour were observed, the first lines to appear would thus be H and K; then as the partial pressure was increased they would be followed by the other lines.

I think we may here have an explanation of that striking phenomenon which is sometimes seen when observing sun-spots, namely, that some of the lines are distorted, showing rapid motion in the line of sight, while other lines of the same element are not affected at all.

* 'Roy. Soc. Proc.' vol. 16, 1868.

In the case of calcium just cited, let us suppose that in the sun we are looking through a vast depth of say, 50,000 miles of calcium vapour: if a storm were blowing on the upper surface, but only extending to say a depth of 1000 miles, the H and K lines would be distorted, but the other lines in the spectrum which are only produced by the deeper layers would not be affected at all.

If we take a tube containing a transparent gas such as hydrogen, and observe with a spectroscope the light passing through it from a source giving a continuous spectrum, we can see no dark absorption lines due to the gas as in the solar spectrum. And probably we would have to increase the depth of gas to many miles before we would see the lines. In the sun we are able to look through from 10,000 to 100,000 miles of hydrogen, and from the sharpness of the lines in the solar spectrum we have strong evidence that even that great depth of gas is still almost quite transparent. Thus we are led to the possibility that if the sun were expanded into a nebula, say 10 times the diameter of Neptune's orbit, it would give the bright line spectrum still.

Other substances such as sodium become opaque when the thickness of their vapour is comparatively small; this shows how minute on this view the partial pressure of sodium vapour and other vapours like it must be in the solar atmosphere.

It seems thus tenable that the sun's atmosphere consists principally of hydrogen and helium with only minute traces of such substances as sodium.

In the great nebula in Orion it is permissible to suppose that the depth is about equal to the breadth. Its immeasurable distance from us shows us what a stupendous depth of gas lies between us and the stars beyond, and yet their light shows no falling off in brilliancy. This indicates with what extraordinary freedom ordinary light is able to pass through untold millions of miles of hydrogen and helium. It thus seems not improbable, as above urged, that if all the hydrogen at present in the solar system were again expanded into a nebula, say with a diameter of 10 times the orbit of Neptune, it would then, if seen from a distant star, still give a bright line spectrum the same as Orion now gives to us. The volume of a nebula of this size would be of the order of 10^{15} times that of the sun; if the sun were expanded to this size the partial pressures of such substances as sodium, which now in the sun are so small, would become evanescent, and their spectra would probably be quite invisible, so that we can conceive that the solar nebula in its early stages of evolution gave a spectrum quite similar to many others now visible in the heavens. It would thus appear that hydrogen and possibly helium are the principal constituents of the atmospheres of all stars and nebulae, and that most of the other elements are present in much smaller

quantities; and that the spectrum of a star may depend far more on the partial pressures of these elements in the star's atmosphere than on its temperature.

Great caution is needed in regard to assuming that, because certain stars have a spectrum of lines which are only seen in the spark, they must be at a higher temperature than other stars that do not show these lines. We seem to have little direct evidence that would justify us in stating that the spark is hotter than the arc. The conclusion that it is so seems to have been formed mainly because in the spark spectrum we often get more lines, and these are generally more towards the violet. It seems quite conceivable that the abrupt and oscillatory discharge in the spark is able to excite vibrations in the atoms irrespective of the temperature of the gas. At any rate it would be difficult to produce direct experimental evidence showing that in the spark we have a high temperature in the strict sense. In the arc we undoubtedly have a high temperature; but even there, may not atomic disturbances be set up by the electric current, such as would give rise to certain lines in the spectrum which would not be visible if the gas could be heated say in an oven to the same temperature?

Some very interesting experiments bearing on this have been lately recorded by A. S. King.* He repeats some earlier experiments made by Liveing and Dewar, and his work leads him to the following conclusion: "This shift of maximum in the spark towards longer waves, in connection with the behaviour of the caesium series at different temperatures, would point, on its face, to the conclusion that the arc is of a higher temperature than the spark, in contradiction to the view generally held; though our knowledge will not enable us to deny that most of the spark properties usually deduced as evidence of higher temperature,† such as great brightness with small volume, richness of spark spectra in ultra-violet lines, etc., may be the result of the more violent electrical action.‡ However, the modern view points to something so different from a thermal radiation in the spark, that it seems as if the word 'temperature' cannot be used in the same sense for both arc and spark."

If we take a Plücker vacuum-tube containing a trace of air, the most feeble electrical discharge through it will make the gas glow brilliantly and give a

* "On the emission spectra of metals as given by an electric oven," *'Astro-physical Journal,'* April, 1905.

† Liveing and Dewar, *'Roy. Soc. Proc.,'* vol. 44, pp. 241 and 242, 1888.

‡ J. Hartman and G. Eberhard, "On the Occurrence of Spark Lines in Arc Spectra," *'Astro-physical Journal,'* No. 3, p. 229, 1903; J. Hartman, "On a new Relationship between Arc and Spark Spectra," *'Astro-physical Journal,'* No. 4, p. 270, 1903; H. Crew and J. C. Barker, "On the Thermal Development of the Spark Spectrum of Carbon," *'Astro-physical Journal,'* No. 2, p. 61, 1902.

bright line spectrum ; even rubbing the outside of the tube with a cloth will make it glow. But if we send a beam of light from a glowing solid body through the tube when thus excited, we do not see the absorption spectrum of air. Even the depth of our atmosphere is not sufficient to bring out all its absorption lines, as we see an enormous increase in their number when the sun is near the horizon. This appears to be evidence that the electrical discharge is able to make the air give an emission spectrum quite irrespective of its temperature. If it were a temperature effect we ought to get some trace of an absorption spectrum by looking through the tube at a continuous source of light.

If we could *heat* a column of air, of the same depth as our atmosphere, to a temperature sufficiently high to make it radiate waves up to its extreme ultra-violet lines, we would then on the present view get a bright-line spectrum identical with the absorption spectrum we get when the sun is in the zenith ; and if we could heat to the *same temperature* a column of air of the depth that a beam of light traverses when the sun is on the horizon, we would get an enormous increase in the number of bright lines, in the same position and density as the dark lines we observe in the absorption spectrum with a low sun.

If we could reduce gradually the depth of our column of air keeping the temperature the same, we should get less and less bright lines, in the same way as we would get less absorption lines, and ultimately when the depth of the column was sufficiently reduced we would be unable to get either bright lines or dark ones.

As has been pointed out earlier in this paper, substances vary enormously in the density or partial pressure that they require to give an emission or absorption spectrum. A few inches of sodium vapour will give a far darker absorption spectrum than we get in the sun, indicating that the partial pressure of that substance in the solar atmosphere must be of extreme tenuity.

Magnesium vapour is probably very opaque. Some years ago (1895), I was engaged in measuring the thermal radiation from sun-spots with a Boys' radio-micrometer, using a large image of the sun about 3 feet in diameter, which was thrown on a screen in the laboratory by a heliostat. There was a fairly large spot on the disc, and my eye at once detected a brilliant green patch on the side of the umbra and partially covering it. It was shining like a green lamp. I then observed it with the solar spectroscope, and found all the magnesium lines brilliantly reversed. I also took a photograph of it with the photo-heliograph.

The area of this magnesium cloud was probably about 60,000,000 square

miles. It has always seemed very difficult to explain the origin of a cloud like this mainly of one substance only, like magnesium; but if we assume that the partial pressure of magnesium in the solar atmosphere is almost evanescent, the smallest increase of its density would greatly increase the intensity and number of its lines. The reversal of its spectrum merely showed that the vapour was at a much higher temperature in the spot than in the neighbouring photosphere.

If the vapours of the different elements in the sun lie below the photosphere more or less in layers according to their atomic weight, while the reversing layer above the photosphere is made up of a mixture of a great number of them by convection currents, is it not conceivable that some vapours like magnesium get carried up from below and temporarily increase their partial pressure locally in the atmosphere? The quantity of vapour thus required to bring out more enhanced lines in the spectrum would possibly be quite minute.

To summarise this paper; it seems that—

1. If the temperature of a star is sufficiently high to enable the gases, if dense enough, to emit all their lines up to the extreme ultra-violet, then an increase of temperature would have very little effect in altering their spectrum.
 2. Differences in the partial pressure of any one gas in two stars of the *same temperature* may have a very large effect in determining the lines that would be seen in its spectrum.
 3. Stars whose temperatures were slightly above and below the critical point at which the photospheric clouds are formed would differ largely in their spectrum.
 4. From the above causes it would seem impossible to classify stars on a scale of temperature alone.
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Researches on Explosives.—Part III.

By Sir ANDREW NOBLE, Bart., K.C.B., F.R.S., D.Sc., etc.

(Received and Read June 8, 1905.)

(Abstract.)

The principal object of the researches which are communicated in this paper was to ascertain, with as much accuracy as possible, the differences in the transformations which modern explosives suffer when fired under gradually increasing, but considerable, differences of pressure. The first part of the paper gives a description of the varied apparatus which was designed or used in the research.

Although the author has made experiments with many other explosives, those to which attention is devoted in this paper are three in number: (i) the cordite known as Mark I (for which the country is indebted to the labours of Sir F. Abel and Sir James Dewar); (ii) the modified cordite known as M.D.; and (iii) a tubular nitro-cellulose known as R. R. Rottweil.

The modes of observation and calculation followed are shown by several examples, and then in tabular form are given the results of the series of experiments on the three explosives named, which were fired under a variety of densities and pressures, and with regard to which the essential constants have been determined. These tables give:—

1. The densities under which the various charges were fired.
2. The volumes of permanent gases generated, at 0° C. and 760 mm. of barometric pressure, per gramme of explosive.
3. The total volume of gas per gramme, aqueous vapour being included.
4. The percentage volumes of permanent gases.
5. The percentage volumes of the total gases.
6. The percentage weights of the total gases.
7. The pressures at each density in tons per square inch.
8. The same pressures in atmospheres.
9. The units of heat determined, the water being fluid.
10. The units of heat, water being gaseous.
11. The specific heat of the products of explosion for each density.
12. The comparative temperatures of explosion determined by dividing the units of heat (water gaseous) by the specific heats in 11.
13. The comparative potential energy, the highest energy determined being taken as unity.

Cordite Mark I.

Density of charge exploded.

	0·05	0·10	0·15	0·20	0·25	0·30	0·40	0·50
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Volume of permanent gas per gramme.

	678·0	685·1	690·9	711·2	691·9	662·4	644·9	623·6
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Volumes of total gas per gramme.

	877·8	870·7	877·9	888·7	871·3	833·6	820·0	798·8
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Percentage volumes of permanent gases.

CO ₂	27·15	28·05	29·10	30·65	31·75	35·70	38·30	41·95
CO	34·35	33·10	31·90	29·65	28·90	24·80	22·65	19·10
H	17·50	19·25	19·50	19·55	18·95	17·50	14·80	12·05
CH ₄	0·30	0·45	0·60	1·55	1·60	3·30	5·05	7·05
N	20·70	19·15	18·90	18·60	18·80	18·70	19·20	19·85

Percentage volumes of total gases.

CO ₂	20·97	22·06	22·99	24·53	25·25	28·37	30·13	33·02
CO	26·53	26·08	25·20	23·73	22·98	19·71	17·81	15·08
H	13·52	15·14	15·41	15·64	15·07	13·91	11·64	9·48
CH ₄	0·23	0·36	0·47	1·24	1·27	2·62	3·97	5·55
N	15·99	15·06	14·93	14·88	14·95	14·86	15·10	15·62
H ₂ O	22·76	21·35	21·00	19·98	20·48	20·53	21·35	21·30

Percentage weights of total gases.

CO ₂	36·10	38·24	39·62	42·91	42·82	47·03	48·68	51·84
CO	29·00	28·70	27·69	25·51	24·80	20·78	18·32	15·08
H	1·14	1·16	1·21	1·25	1·16	1·04	0·85	0·67
CH ₄	0·18	0·21	0·31	0·79	0·78	1·58	2·34	3·18
N	17·63	16·62	16·37	16·61	16·17	15·68	15·57	15·65
H ₂ O	15·95	15·07	14·80	12·93	14·27	13·89	14·24	13·63

Pressure in tons per square inch.

	2·9	7·8	11·49	17·2	21·08	30·5	41·4	52·9
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Pressure in atmospheres.

	442·1	1189·0	1751·5	2621·9	3213·3	4649·3	6310·8	8063·8
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Units of heat, water fluid.

	1272·3	1250·7	1249·9	1244·2	1242·3	1273·6	1299·7	1360·0
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Units of heat, water gaseous.

	1186·8	1169·9	1170·6	1174·9	1165·8	1199·2	1223·4	1287·0
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Specific heat.

	0·23040	0·22918	0·23005	0·22863	0·22920	0·22804	0·22668	0·22385
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Temperatures of explosion. Centigrade.

	5151°·1	5104°·7	5088°·4	5138°·9	5086°·4	5258°·7	5397°·0	5749°·4
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Comparative potential energy.

	0·9825	0·9822	0·9788	0·9739	0·9689	0·9619	0·9677	1·0000
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M.D. Cordite.

Density of charge exploded.								
	0·05	0·10	0·15	0·20	0·25	0·30	0·40	0·45
Volume of permanent gas per gramme.								
	781·8	788·4	799·9	769·1	745·5	735·0	692·7	676·3
Volumes of total gas per gramme.								
	955·4	946·4	933·8	915·5	888·6	875·3	831·2	810·6
Percentage volumes of permanent gases.								
CO ₂	18·15	20·10	21·50	23·80	26·75	29·40	33·40	36·60
CO	42·60	40·70	38·90	36·30	33·65	31·10	27·25	24·80
H	23·15	23·10	22·70	21·70	19·80	17·75	14·45	11·90
CH ₄	0·35	1·00	1·90	3·40	4·65	6·55	9·30	10·70
N	15·75	15·10	15·00	14·80	15·15	15·20	15·60	16·00
Percentage volumes of total gases.								
CO ₂	14·85	16·74	17·95	19·99	22·45	24·69	27·83	30·56
CO	34·87	33·90	32·48	30·50	28·23	26·12	22·71	20·71
H	18·95	19·24	18·95	18·23	16·61	14·91	12·04	9·94
CH ₄	0·29	0·88	1·59	2·86	3·90	5·50	7·75	8·94
N	12·89	12·57	12·53	12·43	12·71	12·76	13·00	13·36
H ₂ O	18·15	16·72	16·50	15·99	16·10	16·02	16·67	16·49
Percentage weights of total gases.								
CO ₂	27·69	30·82	32·80	36·08	39·30	42·07	45·83	48·75
CO	41·88	39·71	38·11	35·02	31·45	28·32	23·78	21·02
H	1·62	1·61	1·76	1·50	1·32	1·16	0·90	0·72
CH ₄	0·18	0·55	1·06	1·88	2·48	3·41	4·65	5·19
N	15·82	14·74	14·69	14·32	14·19	13·91	13·65	13·59
H ₂ O	13·81	12·57	11·58	11·20	11·26	11·13	11·19	10·73
Pressure in tons per square inch.								
	2·7	6·9	10·2	15·2	20·7	27·62	38·1	43·22
Pressure in atmospheres.								
	411·6	1051·8	1554·8	2317·0	3155·4	4210·3	5807·8	6587·3
Units of heat, water fluid.								
	1035·9	1029·8	1014·7	1034·7	1041·4	1067·2	1150·5	1190·0
Units of heat, water gaseous.								
	961·9	962·4	952·6	974·7	981·1	1007·6	1090·5	1132·5
Specific heat.								
	0·23714	0·23552	0·23840	0·23418	0·23198	0·23082	0·22869	0·22529
Temperatures of explosion. Centigrade.								
	4056°·2	4086°·7	3995°·8	4119°·9	4220°·6	4365°·3	4768°·4	5026°·3
Comparative potential energy.								
	0·8401	0·8282	0·8209	0·8173	0·8215	0·8335	0·8639	0·8842

Nitro-Cellulose.

Density of charge exploded.

0.05	0.10	0.15	0.20	0.222	0.29	0.30	0.40	0.45
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Volume of permanent gas per gramme.

814.7	804.8	804.4	768.9	759.2	737.8	737.9	690.1	680.9
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Volumes of total gas per gramme.

993.1	969.3	970.1	929.9	922.3	883.5	882.2	846.8	816.3
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Percentage volumes of permanent gases.

CO ₂	17.90	19.85	20.85	22.90	25.10	27.85	28.06	33.40	35.00
CO	43.45	41.45	40.65	38.80	36.55	34.30	34.02	27.25	27.85
H	24.40	24.90	23.85	21.75	20.25	17.10	17.16	14.45	12.65
CH ₄	0.60	0.85	1.90	3.50	4.70	7.30	7.41	9.30	11.10
N	13.65	12.95	12.75	13.05	13.40	13.45	13.35	15.60	13.40

Percentage volumes of total gases.

CO ₂	14.68	16.48	17.37	18.94	20.66	23.13	23.47	27.83	29.16
CO	35.63	34.42	33.85	32.08	30.09	28.48	28.46	22.71	23.20
H	20.01	20.67	19.86	17.99	16.67	14.20	14.35	12.04	10.54
CH ₄	0.49	0.71	1.58	2.89	3.87	6.06	6.20	7.75	9.25
N	11.19	10.75	10.62	10.79	11.03	11.17	11.17	13.00	11.16
H ₂ O	18.00	16.97	16.72	17.31	17.68	16.96	16.35	16.67	16.69

Percentage weights of total gases.

CO ₂	26.19	31.08	32.18	34.46	36.88	40.11	40.20	45.83	47.26
CO	43.53	41.24	39.91	37.14	34.15	31.42	30.98	23.78	23.92
H	1.74	1.76	1.68	1.48	1.36	1.12	1.12	0.90	0.79
CH ₄	0.34	0.48	1.07	1.92	2.52	3.82	3.86	4.65	5.45
N	13.71	12.92	12.54	12.52	12.56	12.36	12.35	13.65	11.54
H ₂ O	12.49	12.57	12.62	12.48	12.53	11.17	11.49	11.19	11.04

Pressure in tons per square inch.

3.35	6.26	10.4	14.41	16.47	21.5	20.54	34.9	40.5
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Pressure in atmospheres.

510.7	954.2	1585.3	2196.6	2510.6	3277.4	3181.0	5320.0	6173.6
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Units of heat, water fluid.

896.1	869.8	887.8	929.3	931.0P	970.2P	972.5	1021.4	1036.9
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Units of heat, water gaseous.

829.2	802.4	820.2	862.4	863.9	910.3	910.9	961.4	977.7
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Specific heat.

0.23772	0.23869	0.23871	0.23642	0.23554	0.23126	0.23201	0.22869	0.22828
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Temperatures of explosion. Centigrade.

3488° .1	3361° .7	3435° .9	3647° .8	3667° .7	3936° .2	3926° .1	4203° .9	4282° .9
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Comparative potential energy.

0.7389	0.7251	0.7220	0.7368	0.7438	0.7568	0.7592	0.7659	0.7686
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If the figures given in these tables be carefully examined, it will be observed that for the three explosives the transformation on firing appears, in all, to follow the same general laws.

Thus in all three there is, with increase of pressure, at first a slight increase, afterwards a steady decrease, in the volume of permanent gases produced. This increase, in the total gases, is much less marked with cordite, and in the case of M.D. and nitro-cellulose there is practically a steady decrease in the volume of the total gases.

In all three explosives there is, with increased pressure, a large increase in the volume of carbonic anhydride, and a large decrease in the volume of carbonic monoxide. In the volume of hydrogen this decrease with increase of pressure is very great; while methane, the percentage of which with low pressures is quite insignificant, very rapidly increases, and at the highest density is from 20 to 30 times greater than at the lowest density.

There are some variations in the percentages of nitrogen and water vapour, but on the whole these constituents may be considered to be nearly constant.

The units of heat developed show with increased pressure a slight decline at first, but afterwards increase, and somewhat rapidly at the highest pressures.

In the tables submitted it will be observed that the specific heats and the temperatures of explosion have been given; but with respect to temperatures so far above those in regard to which accurate observations have hitherto been made, the figures given can only be taken as provisional. The specific heats of the various gases have been taken at the values usually assigned to them. Of course, it cannot be assumed that these specific heats remain unchanged over the wide range of temperature necessary, although it has been found that the specific heats of some permanent gases such as nitrogen and oxygen are but slightly altered up to 800° C.

The temperatures of explosion which, as stated, can only be taken as provisional, have been obtained by dividing the units of heat (water gaseous) by the specific heats; although provisional, they can safely be used in comparing the temperatures of explosion of the three explosives. The temperatures of explosion, for example, of cordite and nitro-cellulose at a density of 0.20 may tolerably safely be taken to be in the ratio of 51 to 36.

The author is, from other considerations, inclined to believe that the temperatures obtained, and given in the tables, are not very far removed from the truth. He tried with cordite to confirm the results by using the equation of dilatibility of gases; at the high pressures the results were satisfactory, but quite the reverse at the lower densities.

The comparative approximate potential energies are obtained by multi-

plying the volume of gas produced by the temperature of explosion. The means for the three explosives are respectively : cordite, 0·9762 ; M.D., 0·8387 ; nitro-cellulose, 0·7464. The highest potential energy (taken as unity) it will be noted was obtained from cordite at a density of 0·5.

It is submitted that the wide differences in the transformation of the three explosives with which the experiments have been made, justify the general conclusion at which Sir F. Abel and the writer arrived in the year 1874,* with respect to gunpowder, viz., that any attempt to define by a chemical equation the nature of the metamorphosis which one explosive may be considered to undergo would only be calculated to convey an erroneous impression regarding the *definite nature* of the chemical results and *their uniformity* under different conditions.

The paper continues with a description of the experiments made to determine the time required for the complete ignition of certain explosives, and also other experiments to determine the rate at which the exploded gases part with their heat to the walls of the vessels in which they are confined ; and in conclusion it is pointed out that the experiments made on erosion, with the three explosives referred to in this paper, and with some other explosives, have satisfied the author that the amount of absolute erosion is governed practically entirely by the heat developed by the explosion. It had been thought that pressure would considerably increase the effect of erosion, but in experiments carried on with cordite and nitro-cellulose under pressures varying from 5 tons to 32 tons per square inch, the erosion was practically entirely independent of the pressure both for the cordite and nitro-cellulose. The results of these experiments are graphically given in a plate.

* 'Phil. Trans.,' A, vol. 163, p. 85.

*The Analogy between Lesage's Theory of Gravitation and the
Repulsion of Light.*

By G. H. DARWIN, F.R.S., Plumian Professor and Fellow of Trinity College,
in the University of Cambridge.

(Received May 2,—Read May 18, 1905.)

I am not aware that anyone has taken the trouble to work out Lesage's theory, except in the case where the particles of gross matter, subjected to the bombardment of ultramundane corpuscles, are at a distance apart which is a large multiple of the linear dimensions of either of them. Some years ago I had the curiosity to investigate the case where the particles are near together, and having been reminded of my work by reading Professor Poynting's paper on the pressure of radiation,* I have thought it might be worth while to publish my solution, together with some recent additions thereto.

If a corpuscle of mass m moving with velocity v impinges on a plane surface, so that the inclination of its direction of motion before impact to the normal to the surface is θ , it communicates to the surface normal momentum $kmv \cos \theta$, and tangential momentum $k'mv \sin \theta$; where k is 1 for complete inelasticity, and 2 for perfect elasticity, and k' is 0 for perfect smoothness and 1 for perfect roughness.

In the following paper the effects are investigated of the bombardment by Lesagian corpuscles of two spheres, which are taken to be types of the atoms or molecules of gross matter. The effects of the normal and tangential components of the momentum communicated by each blow from a corpuscle will be treated separately.

§ 1. *The Normal Component of the Impacts.*

Suppose that there are in space n corpuscles per unit volume, moving indiscriminately in all directions with velocity v ; let the mass of each corpuscle be m , and ρ the density of the medium, so that $\rho = mn$.

Suppose, further, that the corpuscles are so small that collisions between them are rare enough to be negligible. The system thus described is that of Lesage's mechanism for explaining gravitation, provided that the corpuscles are not perfectly elastic.

* 'Phil. Trans.,' A, vol. 202, pp. 525—552. I have had the advantage of corresponding with him on the present subject.

As stated in the introductory remarks, when any corpuscle strikes a plane surface at such an angle that θ is the inclination of its motion before impact to the normal to the plane, it communicates to the plane normal momentum $k m v \cos \theta$, where k is a factor lying between 1 and 2, being 1 for perfectly inelastic corpuscles, and 2 for perfectly elastic ones.

If two bodies, A and B , are exposed to the bombardment of corpuscles, the Lesagian attraction between them will vanish if the corpuscles are perfectly elastic, because the corpuscles reflected between A and B will on the whole cause such a repulsion between the bodies as exactly to counterbalance the attraction.

But in the present investigation we shall only consider those corpuscles which come from infinity, and pay no attention to their behaviour after impact on the surfaces of A and B . This can, I suppose, be only completely justified when the corpuscles are perfectly inelastic.

If the velocity of each of the n corpuscles in unit volume be represented by a vector drawn from a centre, the ends of the vectors will lie equally spaced on the surface of a sphere of radius v . If from the centre of the sphere of velocities a cone of small solid angle $\delta\omega$ be drawn, the number of corpuscles per unit volume, whose directions of motion fall within the cone is $n\delta\omega/4\pi$.

Let us consider the pressure on a surface exposed to bombardment. On the surface draw a unit area, which may clearly be treated as plane, and let θ be the zenith distance of the axis of the cone $\delta\omega$. On the unit area draw an oblique prism, with edges of length v , parallel to the axis of the cone $\delta\omega$; the volume of this prism is $v \cos \theta$. Hence the number of corpuscles, whose directions of motion fall within the cone $\delta\omega$, lying inside the oblique prism at any moment is $n v \cos \theta \delta\omega/4\pi$. At the end of unit time elapsing after the moment under consideration all these corpuscles will have struck the plane, and each will have communicated momentum towards the nadir equal to $k m v \cos \theta$. Thus the momentum towards the nadir communicated by this class of corpuscles is $k m n v^2 \cos^2 \theta \delta\omega/4\pi$.

Since $mn = \rho$, the pressure (or momentum towards the nadir communicated per unit time and area) is

$$\frac{k\rho v^2}{4\pi} \sum \cos^2 \theta \delta\omega,$$

where the summation is effected for all directions whence corpuscles may come.

If the particles may come from all over the sky, the summation is for half of angular space, and $\sum \cos^2 \theta \delta\omega = \frac{2}{3}\pi$. Therefore the pressure p on the surface is given by

$$p = \frac{1}{6} k \rho v^2.$$

If we put $k = 2$, this is the well-known result of the kinetic theory of gases.

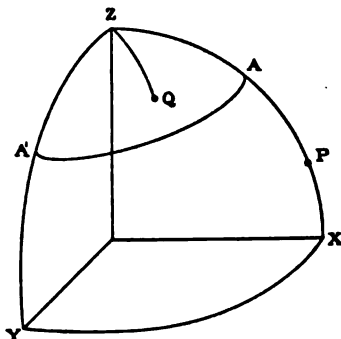
If, however, a certain cone of space is screened off, so that no corpuscle can come from thence, the pressure is given by

$$p = \frac{1}{6}kpv^2 - \frac{kpv^2}{4\pi} \sum \cos^2 \mathfrak{S} \delta\omega,$$

where the summation is taken over the screening area.

In fig. 1 let the origin be at the unit area, and let P be the intersection with the celestial sphere of the normal to the area; let the screen be circular

FIG. 1.



round the Z axis, and let AA' be one quadrant of the screen. Let the radius of the screen be α , and the zenith distance (for an observer standing on the unit area) of the centre of the screen be β . Then

$$ZA = ZA' = \alpha, \quad ZP = \beta.$$

Let θ, ϕ be the polar co-ordinates of an element $\sin \theta d\theta d\phi$ of the screen at Q, so that the $\delta\omega$ of the formula for the pressure is $\sin \theta d\theta d\phi$. Also, since the \mathfrak{S} of the formula is the angle PQ, we have

$$\cos \mathfrak{S} = \cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi.$$

Hence, taking the summation over the area of the screen,

$$\begin{aligned} \frac{1}{2\pi} \sum \cos^2 \mathfrak{S} \delta\omega &= \frac{1}{2\pi} \int_0^{2\pi} \int_0^\alpha (\cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi)^2 \sin \theta d\theta d\phi \\ &= \int_0^\alpha (\cos^2 \theta \cos^2 \beta + \frac{1}{2} \sin^2 \theta \sin^2 \beta) \sin \theta d\theta \\ &= \int_0^\alpha [(\frac{2}{3} \cos^2 \beta - \frac{1}{2}) \cos^2 \theta + \frac{1}{2} \sin^2 \beta] \sin \theta d\theta \\ &= \frac{1}{2} (\cos^2 \beta \cos \alpha \sin^2 \alpha + \frac{2}{3} + \frac{1}{3} \cos^2 \alpha - \cos \alpha). \end{aligned} \quad (1)$$

Thus

$$p = \frac{1}{6}kpv^2 - \frac{1}{4}kpv^2 (\cos^2 \beta \cos \alpha \sin^2 \alpha + \frac{2}{3} + \frac{1}{3} \cos^2 \alpha - \cos \alpha).$$

same all round the sphere, and it cannot contribute anything to the resultant force; hence it may be omitted.

Since the expression for the pressure does not involve ϕ , the integration with respect to ϕ simply introduces the factor 2π . Thus the resultant force estimated towards B , in as far as it is due to the elements from which B is wholly visible, is

$$\frac{1}{2}\pi k\rho a^2 v^2 \int [\cos^2 \beta \cos \alpha \sin^2 \alpha + \frac{2}{3} + \frac{1}{3} \cos^2 \alpha - \cos \alpha] \cos \theta \sin \theta d\theta,$$

where the limits of θ are $\cos^{-1}\left(\frac{a+b}{R}\right)$ and 0.

This expression may be integrated rigorously, but it would not be expedient to do so, because the result is very complicated, and because I have failed to obtain a rigorous integral for the remaining portion of the complete expression, namely, where B is only partially visible.

It will now save trouble if we omit the factor $\frac{1}{2}\pi k\rho a^2 v^2$ and reintroduce it later, and if besides we choose R as our unit of length.

Hence we have

$$\sin \alpha = \frac{b}{r}, \quad \sin \beta = \frac{1}{r} \sin \theta, \quad \cos \beta = \frac{\cos \theta - a}{r}, \quad r^2 = 1 + a^2 - 2a \cos \theta,$$

and the limits of θ are $\cos^{-1}(a+b)$ to 0.

$\cos \alpha$ can be expanded convergently in powers of b/r , so long as the two spheres do not actually touch, and we easily obtain

$$\frac{2}{3} - \frac{1}{3} \cos^2 \alpha - \cos \alpha = \frac{1}{2} \frac{b^4}{r^4} + \frac{1}{12} \frac{b^6}{r^6} + \frac{1}{84} \frac{b^8}{r^8} + \dots,$$

$$\sin^2 \alpha \cos \alpha = \frac{b^3}{r^3} - \frac{1}{2} \frac{b^4}{r^4} - \frac{1}{8} \frac{b^6}{r^6} - \frac{1}{16} \frac{b^8}{r^8} - \dots,$$

also
$$\cos^2 \beta = \frac{1}{r^2} (\cos^2 \theta - 2a \cos \theta + a^2).$$

Hence the integral becomes

$$\int \left(\frac{b^3}{r^3} - \frac{1}{2} \frac{b^4}{r^4} - \frac{1}{8} \frac{b^6}{r^6} \dots \right) (\cos^2 \theta - 2a \cos \theta + a^2) \cos \theta \sin \theta d\theta \\ + \frac{1}{2} b^2 \int \left(\frac{b^2}{r^4} + \frac{1}{2} \frac{b^4}{r^6} + \frac{1}{12} \frac{b^6}{r^8} \dots \right) \cos \theta \sin \theta d\theta.$$

Now $r^2 = (1 + a^2) \left(1 - \frac{2a}{1 + a^2} \cos \theta \right).$

If, then, we write

$$A_1 = \frac{2a}{1 + a^2}, \quad B_{2n} = \frac{b^{2n}}{(1 + a^2)^{n+1}},$$

we have

$$r^2 = (1 + a^2) (1 - A_1 \cos \theta).$$

Whence

$$\frac{b^{2n}}{r^{2n+2}} = B_{2n} \left\{ 1 + (n+1) A_1 \cos \theta + \frac{(n+1)(n+2)}{1.2} A_1^2 \cos^2 \theta + \dots \right\}.$$

Integrating between the appropriate limits, we find

$$\begin{aligned} \int \frac{b^{2n}}{r^{2n+2}} \cos^m \theta \sin \theta d\theta &= B_{2n} \left\{ \frac{1}{m+1} + \frac{n+1}{m+2} A_1 + \frac{(n+1)(n+2)}{1.2(m+3)} A_1^2 + \dots \right\} \\ &- B_{2n} \left\{ \frac{(a+b)^{m+1}}{m+1} + \frac{n+1}{m+2} A_1 (a+b)^{m+2} \right. \\ &\quad \left. + \frac{(n+1)(n+2)}{1.2(m+3)} A_1^2 (a+b)^{m+3} + \dots \right\}. \end{aligned}$$

It will be observed that the suffixes of the B 's and of A_1 indicate their orders in the powers of $1/R$.

This formula may be applied to each term of the preceding integrals, so that the result may be obtained in terms of A_1 and B_{2n} .

The several terms must then be expanded in powers of a^2 , and terms rearranged in their several orders.

After some tedious analysis I find, on reintroducing R , which was treated as being the unit of length, the following result as far as the ninth order:—

$$\begin{aligned} \frac{1}{2} \pi k \rho \frac{v^2 a^2 b^2}{R^2} &\left\{ 1 + \frac{8}{3.5} \frac{a}{R} + \frac{4a(4a^2 + 7b^2)}{3.5.7R^3} + \frac{a(8a^4 + 36a^2b^2 + 21b^4)}{3.5.7R^5} \right. \\ &\quad + \frac{a}{R^7} \left(\frac{3^2}{8.9.3} a^6 + \frac{8}{3.1} a^4 b^2 + \frac{4}{3} a^2 b^4 + \frac{1}{6} b^6 \right) \\ &\quad \left. - \frac{7b^2}{R^4} \left(\frac{1}{3} a + \frac{5}{4} b \right) - \frac{2b^2}{R^6} \left(\frac{1}{3} a^3 + \frac{3}{8} a^2 b + \frac{1}{6} a b^2 - \frac{3}{16} b^3 \right) \right\}. \end{aligned} \quad (2)$$

This formula gives the force on the sphere A towards B in so far as it is produced by the normal component of the bombardment on those parts of A from which B is completely visible. It remains to investigate the regions whence B is only partially visible.

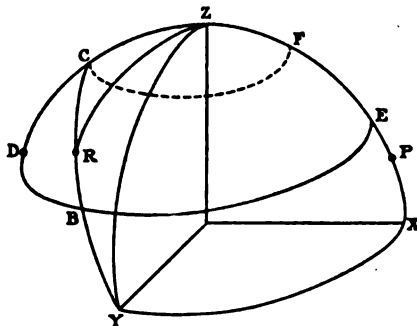
In fig. 3, as in fig. 1, let the origin be at a unit area on sphere A , and let P be the intersection of the normal to the area with the celestial sphere. Then if PC is a right-angle, CY will be the horizon which bounds the screen. Let Z be the axis of the screening cone, and DBE the cone itself. As in the previous case, the semi-angle of the cone is denoted by α , and PZ is β .

The half of the screen which is shown in the figure is $CBEZ$.

If Q be any point in the screen, the pressure on the unit area on the sphere A is

$$\frac{1}{2} k \rho v^2 - \frac{k \rho v^2}{4\pi} \sum \cos^2 PQ d\omega,$$

FIG. 3.



the summation being carried out over the whole screen. As before, we may neglect the constant part of the expression for the pressure.

In this figure more than half the sphere B is visible, and the case when less than half is visible will be treated subsequently.

If θ, ϕ are the polar co-ordinates of Q ,

$$\frac{1}{2\pi} \Sigma \cos^2 PQ \delta\omega = \frac{1}{2\pi} \iint (\cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi)^2 \sin \theta d\theta d\phi,$$

where the integral is taken over the area $CBEZ$ and the other half not shown in the figure.

The area of integration may conveniently be divided into two parts—viz., the part inside the dotted circle and the part between CF and BE .

The part of the result corresponding to the dotted circle may be obtained at once from our previous result (1), for CZ the radius of the cone is equal to $\frac{1}{2}\pi - \beta$, and therefore the result is

$$\frac{1}{2} \{ \cos^4 \beta \sin \beta + \frac{2}{3} + \frac{1}{3} \sin^3 \beta - \sin \beta \}.$$

For the remaining portion, take the limits of integration so as only to include $CBEF$; then doubling the preceding formula, so as to permit us to halve the range of ϕ , we write the integral in the form

$$\begin{aligned} \frac{1}{\pi} \iint (\cos^2 \theta \cos^2 \beta + \frac{1}{2} \sin^2 \theta \sin^2 \beta + \frac{1}{2} \sin^2 \theta \sin^2 \beta \cos 2\phi \\ + 2 \sin \theta \cos \theta \sin \beta \cos \beta \cos \phi) \sin \theta d\theta d\phi. \end{aligned}$$

If R is any point on the boundary CB in colatitude θ , its longitude ϕ is equal to $\pi - CZR$; also $CZ = \frac{1}{2}\pi - \beta$. Then from the right-angled spherical triangle CZR we have

$$\cos \phi = -\cot \beta \cot \theta.$$

Thus the limits of ϕ are $\cos^{-1} [-\cot \beta \cot \theta]$ to 0; and the limits of θ are α to $\frac{1}{2}\pi - \beta$.

At the upper limit of ϕ we have

$$\sin \phi = \sqrt{(1 - \cot^2 \beta \cot^2 \theta)} = \frac{\sqrt{(\sin^2 \theta - \cos^2 \beta)}}{\sin \beta \sin \theta},$$

and $\sin 2\phi = -2 \frac{\cos \beta \cos \theta}{\sin^2 \beta \sin^2 \theta} \sqrt{(\sin^2 \theta - \cos^2 \beta)}.$

Integrating with respect to ϕ , we obtain

$$\begin{aligned} & \frac{1}{\pi} \int (\cos^2 \theta \cos^2 \beta + \frac{1}{2} \sin^2 \theta \sin^2 \beta) \cos^{-1} (-\cot \beta \cot \theta) d\theta \\ & - \frac{1}{2\pi} \int \cos \beta \cos \theta \sqrt{(\sin^2 \theta - \cos^2 \beta)} \sin \theta d\theta \\ & + \frac{2}{\pi} \int \cos \beta \cos \theta \sqrt{(\sin^2 \theta - \cos^2 \beta)} \sin \theta d\theta. \end{aligned}$$

The last two terms involve the same integral and only differ in the coefficients; they therefore fuse together with a coefficient $3/2\pi$.

The whole may now be written

$$\begin{aligned} & -\frac{1}{\pi} \int \cos^{-1} (-\cot \beta \cot \theta) \frac{d}{d\theta} [\frac{1}{3} \cos^3 \theta (\frac{3}{2} \cos^2 \beta - \frac{1}{2}) + \frac{1}{2} \sin^2 \beta \cos \theta] d\theta \\ & + \frac{3}{2\pi} \int \sin \theta \cos \theta \cos \beta \sqrt{(\sin^2 \theta - \cos^2 \beta)} d\theta. \end{aligned}$$

The last term is a perfect integral, and the first may be integrated by parts. Effecting this, I find that the indefinite integral of the whole is

$$\begin{aligned} & -\frac{1}{2\pi} \cos \theta [\cos^2 \theta (\cos^2 \beta - \frac{1}{2}) + \sin^2 \beta] \cos^{-1} (-\cot \beta \cot \theta) + \frac{1}{3\pi} \sin^{-1} \frac{\cos \beta}{\sin \theta} \\ & + \frac{\cos \beta}{2\pi} (\sin^2 \theta - \frac{1}{2}) \sqrt{(\sin^2 \theta - \cos^2 \beta)}. \end{aligned}$$

Then taking the expression, between limits, and adding the part corresponding to the dotted circle, we have

$$\begin{aligned} & \frac{1}{2} \sin \beta [\sin^2 \beta (\cos^2 \beta - \frac{1}{2}) + \sin^2 \beta] \\ & - \frac{1}{2\pi} \cos \alpha [\cos^2 \alpha (\cos^2 \beta - \frac{1}{2}) + \sin^2 \beta] \cos^{-1} (-\cot \beta \cot \alpha) \\ & + \frac{1}{3\pi} \sin^{-1} \frac{\cos \beta}{\sin \alpha} - \frac{1}{6} \\ & + \frac{\cos \beta}{2\pi} (\sin^2 \alpha - \frac{1}{2}) \sqrt{(\sin^2 \alpha - \cos^2 \beta)} \\ & + \frac{1}{2} [\cos^4 \beta \sin \beta + \frac{2}{3} + \frac{1}{2} \sin^2 \beta - \sin \beta]. \end{aligned}$$

This expression admits of reduction, and it gives

$$\begin{aligned} \frac{1}{2\pi} \Sigma \cos^2 PQ \delta\omega = & \frac{1}{6} - \frac{1}{2\pi} \cos \alpha [\frac{2}{3} + \sin^2 \alpha (\frac{1}{2} - \cos^2 \beta)] \cos^{-1} (-\cot \beta \cot \theta) \\ & + \frac{1}{2\pi} \cos \beta (\sin^2 \alpha - \frac{1}{2}) \sqrt{(\sin^2 \alpha - \cos^2 \beta)} + \frac{1}{3\pi} \sin^{-1} \frac{\cos \beta}{\sin \alpha}. \quad (3) \end{aligned}$$

The pressure is the same quantity multiplied by $\frac{1}{2}k\rho v^2$.

In the case when less than half of the sphere B is visible, the dotted circle vanishes. It appears that at the upper limit $\theta = \alpha$ at the lower $\theta = \beta - \frac{1}{2}\pi$; the angle $\cos^{-1}(-\cot \beta \cot \theta)$ is the angle ϕ at the point C , and therefore vanishes; and at the same point $\sin^{-1} \frac{\cos \beta}{\sin \theta}$ is equal to $-\frac{1}{2}\pi$. It is, then easily verified that the formula (3) holds good, and we may therefore apply it both when more and when less than half of B is visible.

If p is the pressure as given by this formula, and $a^2 \sin \theta d\theta d\phi$ is the element of area of the sphere A , the component of pressure in the direction AB is $-p \cos \theta \cdot a^2 \sin \theta d\theta d\phi$. This has to be integrated over the "sunset" region of the sphere A . The integration with respect to ϕ is effected at once, and we are left with

$$-2\pi a^2 \int p \sin \theta \cos \theta d\theta,$$

integrated from $\theta = \cos^{-1} \frac{a-b}{R}$ to $\theta = \cos^{-1} \frac{a+b}{R}$, or from $\cos^{-1}(a-b)$ to $\cos^{-1}(a+b)$, when R is taken as the unit of length.

We have accordingly to multiply (3) by $\pi k \rho a^2 v^2 \sin \theta \cos \theta d\theta$ and integrate it from $\theta = \cos^{-1}(a-b)$ to $\cos^{-1}(a+b)$.

I have not been able to effect the integration rigorously, and shall not give the full details of the tedious analysis involved in the approximate integration.

It is convenient, in the first place, to change the independent variable.

Putting then $\sin \psi = \frac{a - \cos \theta}{b}$, so that the limits become $\pm \frac{1}{2}\pi$, we have

$$\sin \theta \cos \theta d\theta = (ab \cos \psi - b^2 \sin \psi \cos \psi) d\psi,$$

$$r^2 = 1 - a^2 + 2ab \sin \psi, \quad \cos \beta = -\frac{b}{r} \sin \psi = -\sin \alpha \sin \psi,$$

so that

$$\psi = -\sin^{-1} \frac{\cos \beta}{\sin \alpha}, \quad \sqrt{(\sin^2 \alpha - \cos^2 \beta)} = \frac{\cot \psi}{\cos \alpha}.$$

If we drop the factor $\pi k \rho a^2 v^2$ temporarily, it will be found that the subject of integration may be written in the form

$$\begin{aligned} & \frac{1}{4}b^4(1+2a^2)(\frac{1}{4}+\sin^2 \psi) - \frac{1}{8}b^6(\sin^2 \psi - \frac{1}{4}) + \frac{2}{\pi}ab^5 \psi \sin \psi (\frac{1}{4}+\sin^2 \psi) \\ & + \frac{1}{6\pi}ab^5 \sin^2 \psi \cos \psi (2\sin^2 \psi + 13). \\ & - ab^5 \sin \psi (\frac{1}{4}+\sin^2 \psi) - \frac{1}{2\pi} \psi \{b^4(1+2a^2)(\frac{1}{4}+\sin^2 \psi) - \frac{1}{2}b^6(\sin^2 \psi - \frac{1}{4})\} \\ & - \frac{1}{24\pi}b^4(1+2a^2) \sin \psi \cos \psi (2\sin^2 \psi + 13) \\ & + \frac{b^6}{3\pi} \sin \psi \cos \psi (\frac{1}{8} + \frac{3}{8}\sin^2 \psi - \frac{1}{8}\sin^4 \psi), \end{aligned}$$

multiplied by $(ab \cos \psi - b^2 \sin \psi \cos \psi) d\psi$.

The first two lines of the first factor are even functions of ψ , and the last three lines are odd functions; the first term of the second factor is even, and the second term is odd. Then since the limits of ψ are $\pm \frac{1}{2}\pi$, it follows that we need only multiply the first two lines of the first factor by $ab \cos \psi d\psi$ and the last three lines by $-b^2 \sin \psi \cos \psi d\psi$. All the integrals involved are then known, viz.:—

$$\begin{aligned}\int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi} \sin^{2n} \psi \cos \psi d\psi &= \frac{2}{2n+1}, \\ \int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi} \psi \sin \psi \cos \psi d\psi &= \frac{1}{4}\pi, \\ \int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi} \psi \sin^3 \psi \cos \psi d\psi &= \frac{5}{32}\pi, \\ \int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi} \sin^{2n} \psi \cos^{2m} \psi d\psi &= \frac{(2n-1)(2n-3)\dots 3 \cdot 1}{(2m+2n)(2m+2n-2)\dots 2} \pi.\end{aligned}$$

By means of these I find that the component force on the sphere A from A towards B due to this pressure is

$$\frac{1}{8}\pi k\rho \frac{v^2 a^2 b^2}{R^2} \left\{ \frac{7b^3}{R^4} \left(\frac{1}{3}a + \frac{1}{24}b \right) + \frac{2b^3}{R^6} \left(\frac{1}{3}a^3 + \frac{1}{8}a^2b + \frac{1}{48}ab^2 - \frac{1}{160}b^3 \right) \right\}.$$

Now on comparing this with the expression for the first part of the force in (2) we see that it exactly annuls the terms of the sixth and eighth orders; and we may feel confident that the term of the tenth order would be similarly annulled. The result is of so simple a character that it must surely be possible to prove it in some shorter way. However this may be, our final result for the resultant force on A towards B , which I may call F_A , is given by

$$F_A = \frac{1}{8}\pi k\rho \frac{v^2 a^2 b^2}{R^2} \left\{ 1 + \frac{8a}{15R} + \frac{4a(4a^2 + 7b^2)}{105R^3} + \frac{a(8a^4 + 36a^2b^2 + 21b^4)}{105R^5} + \frac{a}{R^7} \left(\frac{1}{80}a^3a^6 + \frac{1}{24}a^4b^2 + \frac{1}{4}a^2b^4 + \frac{1}{8}b^6 \right) \right\}. \quad (4)$$

We may observe that, as a rough approximation,

$$F_A = \frac{1}{8}\pi k\rho \frac{v^2 a^2 b^2}{(R - \frac{1}{5}a)^2}.$$

By symmetry the full expression for the force on B towards A is

$$F_B = \frac{1}{8}\pi k\rho \frac{v^2 a^2 b^2}{R^2} \left\{ 1 + \frac{8b}{15R} + \frac{4b(4b^2 + 7a^2)}{105R^3} + \frac{b(8b^4 + 36a^2b^2 + 21a^4)}{105R^5} + \dots \right\}.$$

In considering the excess of F_A above F_B , it will suffice if we drop the terms of the seventh and ninth orders, since the reader will easily be able to extend the result if he desires to do so.

Then $F_A - F_B = \frac{1}{8}\pi k\rho \frac{v^2 a^2 b^2}{R^3} \cdot \frac{8}{15} \left(\frac{a-b}{R} \right) \left[1 + \frac{4a^2 - 3ab + 4b^2}{14R^2} \right].$

It follows, therefore, that, as the result of the normal component of the bombardment, the larger sphere is more strongly urged towards the smaller than the smaller towards the larger.

§ 2. *The Tangential Component of the Impacts; Effect of both Components together.*

When a corpuscle m strikes a plane surface so that \mathfrak{J} is the inclination of its motion before impact to the normal to the plane, the tangential component of its momentum is $mv \sin \mathfrak{J}$, and it communicates to the plane tangential momentum equal to $k'mv \sin \mathfrak{J}$, where k' lies between 0 and 1, being 1 for perfect roughness and 0 for perfect smoothness of the surface.

Following a procedure exactly similar to that adopted previously, we see that the corpuscles whose direction of motion before impact lie in a small cone of solid angle $\delta\omega$ communicate a tangential force to the plane equal to

$$\frac{k'\rho v^2}{4\pi} \sin \mathfrak{J} \cos \mathfrak{J} \delta\omega.$$

Let l, m, n be the direction cosines of the normal to the plane bombarded, and l', m', n' the direction cosines of the axis of the cone $\delta\omega$. Then the direction cosines of the projection of the axis of the cone on the plane, which is identical with but opposite in direction to that of the tangential force communicated to the plane, are

$$\frac{l' - l \cos \mathfrak{J}}{\sin \mathfrak{J}}, \quad \frac{m' - m \cos \mathfrak{J}}{\sin \mathfrak{J}}, \quad \frac{n' - n \cos \mathfrak{J}}{\sin \mathfrak{J}}.$$

Hence if X, Y, Z are the components of the force thus imparted to the plane by the bombardment,

$$X = -\frac{1}{4\pi} k'\rho v^2 \Sigma \cos \mathfrak{J} (l' - l \cos \mathfrak{J}) \delta\omega, \quad Y = -\frac{1}{4\pi} k'\rho v^2 \Sigma \cos \mathfrak{J} (m' - m \cos \mathfrak{J}) \delta\omega, \\ Z = -\frac{1}{4\pi} k'\rho v^2 \Sigma \cos \mathfrak{J} (n' - n \cos \mathfrak{J}) \delta\omega,$$

where the summations are carried out over all the directions from whence corpuscles arrive at the plane.

If corpuscles come from all over the sky, $X = Y = Z = 0$; hence the forces are

$$X = \frac{1}{4\pi} k'\rho v^2 \Sigma \cos \mathfrak{J} (l' - l \cos \mathfrak{J}) \delta\omega, \text{ and two others,}$$

where the summations are carried out over the screening area.

In fig. 1 the direction cosines of the normal to the bombarded surface are

$$l = \sin \beta, \quad m = 0, \quad n = \cos \beta;$$

$$\text{and} \quad l' = \sin \theta \cos \phi, \quad m' = \sin \theta \sin \phi, \quad n' = \cos \theta;$$

$$\cos \mathfrak{J} = \cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi.$$

The limits of integration are

$$\phi = 2\pi \text{ to } 0, \quad \theta = \alpha \text{ to } 0, \quad \text{and} \quad \delta\omega = \sin \theta \, d\theta \, d\phi.$$

Therefore

$$X = \frac{1}{4\pi} k' \rho v^2 \int_0^{2\pi} \int_0^\alpha [\sin \theta \cos \phi (\cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi) \\ - \sin \beta (\cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi)^2] \sin \theta \, d\theta \, d\phi,$$

$$Y = \frac{1}{4\pi} k' \rho v^2 \int_0^{2\pi} \int_0^\alpha \sin \theta \sin \phi (\cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi) \sin \theta \, d\theta \, d\phi,$$

$$Z = \frac{1}{4\pi} k' \rho v^2 \int_0^{2\pi} \int_0^\alpha [\cos \theta (\cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi) \\ - \cos \beta (\cos \theta \cos \beta + \sin \theta \sin \beta \cos \phi)^2] \sin \theta \, d\theta \, d\phi.$$

Integrating with respect to ϕ , we find

$$X = \frac{1}{2} k' \rho v^2 \sin \beta \cos^2 \beta \int_0^\alpha \left(\frac{1}{2} - \frac{3}{2} \cos^2 \theta \right) \sin \theta \, d\theta \\ = -\frac{1}{4} k' \rho v^2 \sin \beta \cos^2 \beta \sin^2 \alpha \cos \alpha,$$

$$Y = 0,$$

$$Z = \frac{1}{2} k' \rho v^2 \sin^2 \beta \cos \beta \int_0^\alpha \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \sin \theta \, d\theta \\ = \frac{1}{4} k' \rho v^2 \sin^2 \beta \cos \beta \sin^2 \alpha \cos \alpha.$$

In fig. 2 P is at the bombarded element of surface, and is the origin of fig. 1; then we take PB as the axis of Z , and the dotted line PX as the axis of X . Accordingly the component force in the direction A to B is

$$Z \cos (\beta - \theta) + X \sin (\beta - \theta) = \frac{1}{4} k' \rho v^2 \sin \beta \cos \beta \sin^2 \alpha \cos \alpha \sin \theta. \quad (5)$$

The element of surface at P is $\alpha^2 \sin \theta \, d\theta \, d\phi$, and it is to be noted that θ is used in a different sense from that employed in evaluating X , Y , Z .

Hence the total force on the sphere A from A to B , due to the tangential component arising from the bombardment, for all those parts of A from which B is wholly visible, is

$$\frac{1}{4} k' \rho v^2 \alpha^2 \iint \sin \beta \cos \beta \sin^2 \alpha \cos \alpha \sin \theta \cdot \sin \theta \, d\theta \, d\phi,$$

the limits of ϕ being 2π to 0 , and of θ from $\cos^{-1}(\alpha + b)/R$ to 0 .

The integration for ϕ involves only multiplication by 2π .

As before, I take temporarily R as unit of length, so that the limits of θ are $\cos^{-1}(\alpha + b)$ to 0 .

Then

$$\sin^2 \alpha \cos \alpha = \frac{b^2}{r^2} - \frac{1}{2} \frac{b^4}{r^4} - \frac{1}{8} \frac{b^6}{r^6} \dots, \quad \sin \beta \cos \beta = \frac{1}{r^2} \sin \theta (\cos \theta - a).$$

Hence the integral becomes

$$\frac{1}{2} \pi k' \rho v^2 a^2 \int \left(\frac{b^2}{r^2} - \frac{1}{2} \frac{b^4}{r^4} - \frac{1}{8} \frac{b^6}{r^6} \dots \right) \sin^2 \theta (\cos \theta - a) d\theta.$$

If we use the same abbreviations as before in the development in inverse powers of r , and note that

$$\int \sin^2 \theta \cos^{m+1} \theta d\theta = \frac{2}{(m+2)(m+4)} - \frac{(a+b)^{m+2}}{m+2} + \frac{(a+b)^{m+4}}{m+4},$$

we find

$$\begin{aligned} \int \frac{b^{2m}}{r^{2m+2}} \sin^2 \theta \cos \theta d\theta &= B_{2m} \left\{ \frac{2}{2 \cdot 4} + \frac{(n+1)}{1!} \frac{2}{3 \cdot 5} A_1 + \frac{(n+1)(n+2)}{2!} \frac{2}{4 \cdot 6} A_1^2 \right. \\ &\quad \left. + \frac{(n+1)(n+2)(n+3)}{3!} \frac{2}{5 \cdot 7} A_1^3 + \dots \right. \\ &\quad \left. - \frac{(a+b)^2}{2} - \frac{(n+1)}{1!} \frac{(a+b)^3}{3} A_1 - \frac{(n+1)(n+2)}{2!} \frac{(a+b)^4}{4} A_1^2 \right. \\ &\quad \left. - \dots \right. \\ &\quad \left. + \frac{(a+b)^4}{4} + \frac{(n+1)}{1!} \frac{(a+b)^5}{5} A_1 + \frac{(n+1)(n+2)}{2!} \frac{(a+b)^6}{6} A_1^2 \right. \\ &\quad \left. + \dots \right\} \\ \int \frac{b^{2m}}{r^{2m+2}} \sin^2 \theta d\theta &= B_{2m} \left\{ \frac{2}{1 \cdot 3} + \frac{(n+1)}{1!} \frac{2}{2 \cdot 4} A_1 + \frac{(n+1)(n+2)}{2!} \frac{2}{3 \cdot 5} A_1^2 + \dots \right. \\ &\quad \left. - \frac{(a+b)}{1} - \frac{(n+1)}{1!} \frac{(a+b)^2}{2} A_1 - \frac{(n+1)(n+2)}{2!} \frac{(a+b)^3}{3} A_1^2 \right. \\ &\quad \left. - \dots \right. \\ &\quad \left. + \frac{(a+b)^3}{3} + \frac{(n+1)}{1!} \frac{(a+b)^4}{4} A_1 + \frac{(n+1)(n+2)}{2!} \frac{(a+b)^5}{5} A_1^2 \right. \\ &\quad \left. + \dots \right\}. \end{aligned}$$

These formulæ may be applied to each term of the integral, and the result is thus obtained in terms of A_1 and B_{2m} . We next expand these in powers of a^2 , and rearrange the result in their several orders. Finally on reintroducing R I find the following result:—

$$\begin{aligned} \frac{1}{2} \pi k' \rho \frac{v^2 a^2 b^2}{R^2} \left\{ 1 - \frac{8}{3 \cdot 5} \frac{a}{R} - \frac{4a(4a+7b)}{3 \cdot 5 \cdot 7 R^2} - \frac{a(8a^4+36a^2b^2+21b^4)}{3 \cdot 5 \cdot 7 R^5} \right. \\ \left. - \frac{a}{R^2} \left(\frac{3 \cdot 2}{3 \cdot 5 \cdot 7} a^3 + \frac{8}{3} a^2 b^2 + \frac{4}{3} a^2 b^4 + \frac{1}{6} b^6 \right) \right. \\ \left. - \frac{1}{2} \frac{b^2}{R^2} - \frac{b^2}{R^4} \left(\frac{1}{2} a^2 + \frac{2}{3} ab - \frac{1}{8} b^2 \right) - \frac{b^2}{R^6} \left(\frac{1}{2} a^4 + \frac{1}{3} a^2 b^2 + \frac{1}{12} a^2 b^4 - \frac{2}{3} ab^3 + \frac{1}{18} b^6 \right) \right\}. \end{aligned} \quad (6)$$

This gives the force on the sphere A towards B as arising from the tangential component of the impacts, in so far as it is due to those parts of A from which B is completely visible. It remains to consider the regions whence B is only partially visible.

By proceeding in the same way as before I find, for the portion of the result which does not involve that part of the screen which is represented by the dotted circle in fig. 3, after the integration with respect to ϕ ,

$$X = \frac{1}{2\pi} k' \rho v^2 \int_{\frac{1}{2}\pi-\beta}^{\pi} [\sin \beta \cos^2 \beta (\frac{1}{2} - \frac{3}{2} \cos^2 \theta) \cos^{-1}(-\cot \beta \cot \theta) \\ + \cot \beta (\frac{1}{2} - \frac{3}{2} \sin^2 \beta) \cos \theta \sqrt{(\sin^2 \theta - \cos^2 \beta)}] \sin \theta d\theta.$$

$$Z = \frac{1}{2\pi} k' \rho v^2 \int_{\frac{1}{2}\pi-\beta}^{\pi} [\sin^2 \beta \cos \beta (\frac{3}{2} \cos^2 \theta - \frac{1}{2}) \cos^{-1}(-\cot \beta \cot \theta) \\ + (1 - \frac{3}{2} \cos^2 \beta) \cos \theta \sqrt{(\sin^2 \theta - \cos^2 \beta)}] \sin \theta d\theta.$$

The last terms in each of these expressions are integrable as they stand, and for the first terms of each

$$\int (\frac{3}{2} \cos^2 \theta - \frac{1}{2}) \cos^{-1}(-\cot \beta \cot \theta) d\theta \\ = \frac{1}{2} \sin^2 \theta \cos \theta \cos^{-1}(\cot \beta \cot \theta) + \frac{1}{2} \cos \beta \sqrt{(\sin^2 \theta - \cos^2 \beta)}.$$

In proceeding to the limits, it is to be noted that $\cos^{-1}(-\cot \beta \cot \theta)$ is π , when $\theta = \frac{1}{2}\pi - \beta$. Thus after integration we shall have, for that portion which depends on the term involving $\cos^{-1}(-\cot \beta \cot \theta)$, when $\theta = \frac{1}{2}\pi - \beta$,

$$X = +\frac{1}{2\pi} k' \rho v^2 \cdot \frac{\pi}{2} \sin^2 \beta \cos^4 \beta, \quad Z = -\frac{1}{2\pi} k' \rho v^2 \cdot \frac{\pi}{2} \sin^2 \beta \cos^2 \beta.$$

Now, since the resultant force is given by $Z \cos(\beta - \theta) + X \sin(\beta - \theta)$, this portion of the resultant is equal to $-\frac{1}{4} k' \rho v^2 \sin^2 \beta \cos^3 \beta \sin \theta$, where θ has the meaning indicated in fig. 3.

The force due to the portion of the screen represented by the dotted circle is given by the result (5), namely $\frac{1}{4} k' \rho v^2 \sin \beta \cos \beta \sin^2 \alpha \cos \alpha \sin \theta$, when α is put equal to ZC , which is equal to $\frac{1}{2}\pi - \beta$; it is, therefore, equal to $\frac{1}{4} k' \rho v^2 \sin^2 \beta \cos^3 \beta \sin \theta$, and exactly annuls the term referred to above as resulting from the term in $\cos^{-1}(-\cot \beta \cot \theta)$ with $\theta = \frac{1}{2}\pi - \beta$. Thus I find that the complete values for X and Z , inclusive of the dotted circle, are given by

$$X = \frac{1}{4\pi} k' \rho v^2 \{ -\sin \beta \cos^2 \beta \sin^2 \alpha \cos \alpha \cos^{-1}(-\cot \beta \cot \alpha) \\ + \frac{1}{2} \cot \beta [\sin^2 \alpha - \cos^2 \beta - 3 \sin^2 \alpha \sin^2 \beta] \sqrt{(\sin^2 \alpha - \cos^2 \beta)} \} \\ Z = \frac{1}{4\pi} k' \rho v^2 \{ +\sin^2 \beta \cos \beta \sin^2 \alpha \cos \alpha \cos^{-1}(-\cot \beta \cot \alpha) \\ - \frac{1}{2} [\sin^2 \alpha - \cos^2 \beta - 3 \sin^2 \alpha \sin^2 \beta] \sqrt{(\sin^2 \alpha - \cos^2 \beta)} \}.$$

These formulæ may be shown to be equally true of the case where less than half of B is visible, and they are therefore applicable throughout. The component force of A towards B is equal to $Z \cos(\beta - \theta) + X \sin(\beta - \theta)$, and becomes

$$\frac{1}{4\pi} k' \rho v^2 \{ \sin \beta \cos \beta \sin^2 \alpha \cos \alpha \sin \theta \cos^{-1}(-\cot \beta \cot \alpha) - \frac{\sin \theta}{3 \sin \beta} [\sin^2 \alpha - \cos^2 \beta - 3 \sin^2 \alpha \sin^2 \beta] \sqrt{(\sin^2 \alpha - \cos^2 \beta)} \}.$$

In this formula θ is used in the sense indicated by fig. 3.

This expression has to be multiplied by $a^2 \sin \theta d\theta d\phi$, and integrated from $\phi = 2\pi$ to 0, and from $\theta = \cos^{-1}(a-b)/R$ to $\cos^{-1}(a+b)/R$. The integration with respect to ϕ merely involves multiplication by 2π . For the integration with respect to θ , I change the variable to ψ , and, as before, develop the expression and effect the various integrations.

The final outcome of some tedious analysis is that the result is the same as the last three terms of (6) with the sign changed. Hence, when we add this contribution to the force to (6), those three terms simply disappear.

Thus the tangential component of the impacts give as a resultant, say F'_A , acting on the sphere A towards B ,

$$F'_A = \frac{1}{2} \pi k' \rho \frac{v^2 a^2 b^2}{R^2} \left\{ 1 - \frac{8}{3 \cdot 5} \frac{a}{R} - \frac{4a(4a+7b)}{3 \cdot 5 \cdot 7 R^3} - \frac{a(8a^4 + 36a^2 b^2 + 21b^4)}{3 \cdot 5 \cdot 7 R^5} - \frac{a}{R^2} \left(\frac{3 \cdot 3}{8 \cdot 5 \cdot 3} a^6 + \frac{8}{3 \cdot 1} a^4 b^2 + \frac{4}{1} a^2 b^4 + \frac{1}{8} b^6 \right) \right\}. \quad (7)$$

As a rough approximation we have

$$F'_A = \frac{1}{2} \pi k' \rho \frac{v^2 a^2 b^2}{(R + \frac{1}{2} a)^2}.$$

If we form F'_B , or the force acting on the other sphere, it is clear that $F'_A - F'_B$ has a form similar to that found previously for $F_A - F_B$, but it has the opposite sign. Hence, as the result of the tangential component of the bombardment, the larger sphere is less strongly urged towards the smaller one, than the smaller towards the larger.

On comparing (7) with the result for F_A in (4), we see that they only differ in the signs of all the terms after the first, and in the fact that k' replaces k . The result is of so simple a character that it is probable that it may be derived by some elementary considerations which escape me.

Thus, including both the tangential and normal components, we have

$$F_A + F'_A = \frac{1}{2} \pi \rho \frac{v^2 a^2 b^2}{R^2} \left\{ (k+k') + \frac{8}{3 \cdot 5} \frac{a}{R} (k-k') + \frac{4a(4a+7b)}{3 \cdot 5 \cdot 7 R^3} (k-k') + \frac{a(8a^4 + 36a^2 b^2 + 21b^4)}{3 \cdot 5 \cdot 7 R^5} (k-k') + \frac{a}{R^2} \left(\frac{3 \cdot 3}{8 \cdot 5 \cdot 3} a^6 + \frac{8}{3 \cdot 1} a^4 b^2 + \frac{4}{1} a^2 b^4 + \frac{1}{8} b^6 \right) (k-k') \right\}. \quad (8)$$

In the case where the momentum of the impinging corpuscles is completely absorbed by the surface struck, we have $k = k' = 1$, and the force is

$$\frac{1}{2}\pi\rho\frac{v^2a^3b^3}{R^2}.$$

Thus, in this case the force varies rigorously as the inverse square of the distance. No doubt this simple result may be proved much more shortly in the case of the complete absorption of the momentum of impacts.* In any other case the result can only be regarded as approximate, because we have neglected reflected particles. But in general it seems certain that the interaction between the two spheres will not be equal and opposite.

§ 3. *Repulsion of Radiation.*

When the Lesagian corpuscles deliver their whole momentum on impact, we have the exact converse of the case of radiation, for in the one case we consider all the particles which converge on to a given element of surface, and in the other case they all diverge. A corpuscular theory of light would give the same result as the electro-magnetic theory as regards repulsion; hence we see that two radiating and perfectly absorbing spheres at the same temperature will repel one another rigorously as the inverse square of the distance.† The case of a perfectly reflecting sphere which receives radiation

* Such a proof is given in a note to the following section.

† [June 23, 1905.] Professor Larmor has given me a direct proof of the above result. This I paraphrase in my own words as follows:—

A sphere radiating from its surface in the manner of a perfect radiator may be replaced by a uniform distribution of radiating spherules inside it, if we suppose the radiations from the several spherules not to interfere with one another. This follows from the fact that the radiation issuing towards any zenith distance is proportional to the depth of the crowd of spherules beneath it in the given direction. Now for a sphere that depth is a chord of the sphere, and is therefore proportional to the cosine of the zenith distance. Hence the law of radiation of the crowd of spherules is the same as the natural law of radiation from the surface itself.

Suppose that one of the spherules P emits n' corpuscles of mass m with velocity v per unit time, and let it be distant r from the centre A of an absorbing sphere of radius a . With origin at the spherule measure colatitude θ from PA, and longitude from some fixed plane passing through PA.

The number of particles emitted per unit time through solid angle $\sin\theta d\theta d\phi$ is $n' \sin\theta d\theta d\phi/4\pi$. Each of them carries momentum mv , and therefore the component of momentum along PA absorbed per unit time by the sphere A is

$$\frac{n'mv}{4\pi} \sin\theta \cos\theta d\theta d\phi.$$

To find the whole thrust on the sphere A we must integrate thus from $\phi = 2\pi$ to 0, and from $\theta = \sin^{-1} \frac{a}{r}$ to 0.

is analogous to the case treated in § 1, where we consider only the effect of the normal component of the impacts. If two perfectly absorbing spheres have different temperatures, the action and reaction between them will not be equal and opposite. The analogue of this case in the Lesagian hypothesis would be that the velocities of the particles which strike one of the spheres, should be different from those which strike the other.

If one side of a body of any shape be at a higher temperature than the other side, the body will be subject to a force tending to propel the cooler side forward, and to drag the warmer side after it. This follows from the fact that the recoil of the emission on the warmer side is greater than that on the cooler side. The result that a hot sphere will pursue a cold one is a special instance of this more general conclusion.

In the Lesagian hypothesis the pressure has a definite relationship to the amount of energy received per unit area and per unit time, and the law is the same as that which governs the relationship between radiation and the recoil of light. The result has so great a physical interest that it seems

Hence the resultant repulsion exercised by the spherule on the sphere is

$$\frac{1}{2}n'mv \frac{a^2}{r^2}.$$

Now suppose that there are N spherules arranged uniformly in a sphere B , of radius b , whose centre is distant R from the centre of the sphere A .

Since each spherule repels the sphere A inversely as the square of the distance from its centre, it follows, as in the theory of attractions, that the aggregate of them repels inversely as the square of the distance between the centres of the spheres A and B .

Hence the total repulsion of the crowd of spherules must be equal to

$$\frac{1}{2}Nn'mv \frac{a^2}{R^2}.$$

It remains to find the value of Nn' , in terms of the equivalent radiation from the surface of the sphere B .

Nn' is the total number of corpuscles emitted per unit time by the whole crowd, and this must be equal to the total number emitted from the surface of the sphere B .

Now we have taken in the text above n to represent the number of corpuscles emitted from unit area of the surface of the sphere. Hence we have

$$Nn' = 4\pi b^2 n.$$

It follows that the repulsion between the spheres is

$$\pi n m v \frac{a^2 b^2}{R^2}.$$

But it appears from the latter portion of § 3 that

$$nm = \frac{1}{2}\rho v = \frac{1}{2}\rho v.$$

Thus the repulsion is $\frac{1}{4}\pi\rho \frac{v^2 a^2 b^2}{R^2}$ and this is identical with the result obtained at the end of § 2 above.

worth while to investigate this matter more closely. We have already seen in § 1 that the number of Lesagian corpuscles, which strike unit area in unit time is $\Sigma \frac{nv \cos \theta}{4\pi} \delta\omega$, and each corpuscle before impact carries energy $\frac{1}{2}mv^2$. Hence if the surface completely absorbs all the energy on impact, we can at once find I , the total absorption of energy. It is given by

$$I = \iint \frac{1}{2}mv^2 \cdot \frac{nv \cos \theta}{4\pi} \sin \theta \, d\theta \, d\phi = \frac{1}{8}nmv^3.$$

But nm is the mass of the Lesagian medium per unit volume, and has been denoted by ρ , and therefore

$$I = \frac{1}{8}\rho v^3.$$

Complete absorption of energy corresponds to the case $k = 1$, and therefore the Lesagian pressure is $p = \frac{1}{8}\rho v^2$.

Hence
$$p = \frac{4I}{3v}.$$

This result is the converse of the case of a corpuscular theory of radiation, and I is then the radiation of the surface, whilst p is the pressure of radiation.

We shall now see how this same result may be obtained, when the subject is considered from the point of view of radiation.

Suppose that $n \cos \theta \delta\omega / \pi$ be the number of corpuscles of mass m emitted per unit time with velocity v from unit area of a surface through an elementary cone $\delta\omega$ in zenith distance θ . The total number of corpuscles emitted per unit time is n , because

$$\int_0^{2\pi} \int_0^{\pi} \frac{n}{\pi} \cos \theta \sin \theta \, d\theta \, d\phi = n.$$

Each corpuscle carries $\frac{1}{2}mv^2$ energy, and the radiation is given by

$$I = \frac{1}{2}mnv^3.$$

But mn has not the same meaning that it had in § 1, and therefore we must consider what it is.

The number of particles radiated per unit area and time through the elementary cone $\delta\omega$ towards zenith distance θ is $\frac{n \cos \theta}{\pi} \delta\omega$, and therefore

for a small element of area δs it is $\frac{n \cos \theta}{\pi} \delta\omega \delta s$.

We may then concentrate the radiation from δs at its centre, and consider the distribution of corpuscles emitted. Since the corpuscles have mass m and move with velocity v , the total mass of the particles at any moment in an element of volume $r^2 \delta\omega$ distant r from the centre of δs is $\frac{mn}{\pi v} \cos \theta \delta\omega \delta s$.

Hence the density of corpuscles radiated from δs at a point distant r from it, in zenith distance θ , is $\frac{mn \cos \theta}{\pi v r^2} \delta s$.

We may now find the density at a point distant z from an infinite plane radiating surface. Take origin in the plane vertically under the point at which the density is to be found, and let ρ , ϕ be the distance and azimuth of an element of radiating surface. For such an element

$$\delta s = \rho \delta \rho \delta \phi, \quad \cos \theta = \frac{z}{\sqrt{(\rho^2 + z^2)}}, \quad r^2 = \rho^2 + z^2.$$

Then the density at the point under consideration is the sum of the contributions of all elements of the plane, and if we denote that density by σ , we have

$$\sigma = \int_0^{2\pi} \int_0^\infty \frac{mn}{\pi v} \frac{z}{(\rho^2 + z^2)^{\frac{3}{2}}} \rho d\rho d\phi = \frac{2mn}{v}.$$

Hence

$$I = \frac{1}{2} \sigma v^2.$$

The same result will be true infinitely near a curved radiating surface.

We found above in considering Lesagian bombardment that $I = \frac{1}{2} \rho v^2$. Hence it appears that $\sigma = \frac{1}{2} \rho$. This result might have been foreseen, because near the plane half the corpuscles are screened off, and so the density must be half that in free space.

The normal recoil of the radiation is clearly equal to the normal component of the momentum radiated per unit time and area, and therefore

$$p = \int_0^{2\pi} \int_0^{\frac{1}{2}\pi} \frac{n \cos \theta}{\pi} \cdot m v \cos \theta \cdot \sin \theta d\theta d\phi.$$

Completing the integration and substituting for mn its value, we have

$$p = \frac{1}{2} \sigma v^2 = \frac{4I}{3v}.$$

The density of energy in space is clearly $\frac{1}{2} \sigma v^2$, and this is equal to $\frac{2}{3} p$ or $2I/v$.

In the electro-magnetic theory of light the density of energy in space is also $2I/v$, but I understand that the pressure is only half that computed from the corpuscular theory and is equal to $\frac{1}{3} I/v$; thus in that theory the density of energy in space is three times the pressure.

§ 4. *The Resistance to a Sphere moving with Uniform Velocity.*

We may find the force on such a sphere by imparting to the Lesagian corpuscles a uniform drift in superposition on their common velocities v .

Let us first find the pressure on a plane unit area. Take the normal to the area as axis of Z , and suppose that the direction cosines of the axis of an

infinitesimal cone $\delta\omega$ are $\sin \theta \cos \phi$, $\sin \theta \sin \phi$, $\cos \theta$. Then, if U , V , W , are the components of the uniform drift of the corpuscles, the velocity of the corpuscles whose direction of motion is parallel to the axis of the cone is

$$v + U \sin \theta \cos \phi + V \sin \theta \sin \phi + W \cos \theta.$$

The momentum towards the nadir communicated by this class of corpuscles per unit time is therefore

$$\frac{k\rho}{4\pi} (v + U \sin \theta \cos \phi + V \sin \theta \sin \phi + W \cos \theta)^2 \cos^2 \theta \delta\omega.$$

We must then take $\delta\omega = \sin \theta d\theta d\phi$, and integrate through half of angular space. The integration with respect to ϕ may be effected at once, and the expression becomes

$$\begin{aligned} & \frac{1}{2} k\rho \int_0^\pi [v^2 + \frac{1}{2}(U^2 + V^2) \sin^2 \theta + W^2 \cos^2 \theta + 2vW \cos \theta] \cos^2 \theta d\theta \\ &= \frac{1}{2} k\rho \int_0^\pi [v^2 + \frac{1}{2}(U^2 + V^2)(1 - \mu^2) + W^2 \mu^2 + 2vW\mu] \mu^2 d\mu \\ &= \frac{1}{8} k\rho [v^2 + \frac{1}{5}(U^2 + V^2 + W^2) + \frac{3}{8}W^2 + \frac{3}{2}vW]. \end{aligned}$$

Now, suppose a sphere of radius a to be moving with velocity u in the direction of the axis of Z , and that $a^2 \sin \theta d\theta d\phi$ is any element of its surface.

When we reduce the sphere to rest, we have the case just considered, and W of the preceding investigation is equal to $u \cos \theta$. The portion of the pressure corresponding to the terms $v^2 + \frac{1}{5}(U^2 + V^2 + W^2)$ is the same all round the sphere, and will produce no effect; it may, therefore, be omitted.

Then the component of the pressure on the element in the direction of the new axis of Z is

$$\frac{1}{8} k\rho [\frac{3}{5}u^2 \cos^2 \theta + \frac{3}{2}vu \cos \theta] \cos \theta \cdot a^2 \sin \theta d\theta d\phi.$$

This must be integrated all over the sphere. After integration with respect to ϕ , which merely involves multiplication by 2π , we have

$$\begin{aligned} & \frac{1}{4} \pi k\rho a^2 \int_0^\pi (\frac{3}{5}u^2 \cos^2 \theta + \frac{3}{2}vu \cos \theta) \cos \theta \sin \theta d\theta \\ &= \frac{1}{4} \pi k\rho a^2 \int_{-1}^1 \frac{3}{2}vu \mu^2 d\mu = \frac{1}{4} \pi k\rho a^2 vu. \end{aligned}$$

If the whole momentum is absorbed, $k = 1$.

Next consider the tangential component of the momentum. In the investigation of § 2, put $l = 0$, $m = 0$, $n = 1$; $l' = \sin \theta \cos \phi$, $m' = \sin \theta \sin \phi$, $n' = \cos \theta$. Then the components of force are

and I suppose the sphere to be either smooth or rough, and the corpuscles to be either perfectly elastic or inelastic in their collisions.

With perfectly smooth spheres and perfectly elastic corpuscles, it is clear that the total energy of the system remains unchanged when two spheres, immersed in the medium, are made to approach or recede from one another. As no work is done by such movements, there can be no force on either sphere. It would be excessively difficult to prove the vanishing of the force between the two spheres by a detailed examination of the impacts of the corpuscles, because it would be necessary to take into account the corpuscles which are reflected from either sphere so as to strike the other. It is, however, certain that in this case there would be no force, and therefore imperfect elasticity or roughness in the spheres are necessary conditions for the applicability of Lesage's theory.

In the case of partial elasticity and roughness, it would be even more difficult than in the former case to trace the effect of reflected corpuscles which strike the other sphere. But in proportion as the inelasticity and roughness increase, so will a solution, which only takes into account first impacts, increase in accuracy. We may fairly conjecture that a very moderate degree of inelasticity would suffice to make such a solution fairly correct. However this may be, no attempt is made in this paper to consider these repeated impacts.

A fundamental objection to the physical truth of Lesage's hypothesis lies in the fact that it demands a continual creation of energy at infinity to supply the gravific machinery. But Lord Kelvin has suggested a manner in which this physical absurdity might be avoided.* He supposes that the corpuscles are capable of absorbing energy in the form of internal agitation. On each impact some of the energy of translation is converted into energy of agitation, and a repartition of the energies of translation and agitation is effected by the mutual collisions of corpuscles according to Clausius's law. If, however, the work of this paper is correct, this suggestion will not serve to remove all the defects of Lesage's hypothesis.

I here suppose two spheres to be subjected to bombardment, and evaluate the effects of the normal and tangential components of the several impacts separately. It is thus possible to make various hypotheses as to the degrees of elasticity and roughness. It appears that neither the normal nor the tangential components of the impacts give rise to forces of attraction between the spheres which vary rigorously as the inverse square of the distance between their centres. In fact the resultant force acting on one

* "On the Ultramundane Corpuscles of Lesage," 'Phil. Mag.,' May, 1873, vol. 45, p. 321, fourth series.

of the spheres, due to the normal component, varies (approximately) as the inverse square of a distance equal to the distance between the two centres diminished by $\frac{1}{2}$ of the radius of the sphere in question; and the resultant force, due to the tangential component, similarly demands the augmentation of the distance by $\frac{1}{2}$ of the radius of the sphere.

If the two spheres are unequal in size, then, as far as concerns the normal component, the diminution of the distance, so as to maintain the law of inverse square, is greater for the larger sphere than for the smaller; and the like is true for the augmentation in the case of the effect of the tangential component.

It follows that if the normal component is only effective, the larger sphere is more strongly impelled towards the smaller than the smaller to the larger, and the converse is true for the separate action of the tangential component. In general, the sum of the two effects will not insure equality of action and reaction, nor the rigorous truth of the law of the inverse square. If these be necessary conditions for the truth of any theory of gravitation, then Lesage's hypothesis and Lord Kelvin's modification stand condemned. It is true that the inequality of action and interaction may be avoided by supposing that all elementary portions of matter are rigorously of the same size, but this still leaves the law of inverse square imperfectly fulfilled.

There is, however, one limiting case in which these particular imperfections in the theory are avoided. If the inelasticity of the corpuscles is complete and the roughness of the sphere such as absolutely to annul the tangential velocity of a corpuscle on impact—in other words, if the absorption of momentum on impact is total—the law of inverse square becomes rigorous, and action and reaction become equal. This supposition leaves the necessity for the creation of energy at infinity in its acutest form.

The case of the total absorption of energy on impact is strictly analogous to the repulsion of light, for the emission of light may be regarded as the exact converse of Lesage's mechanism. Thus the preceding investigation proves that two radiating and completely absorbing spheres at the same temperature repel one another rigorously as the inverse square of the distance between their centres.

If they are not at the same temperature they will tend to move (as indicated by Poynting) so that the cooler sphere leads. This appears to be a special case of a more general law, namely, that a body with one end hot and the other cold will tend to move with the cold end leading, because the recoil of the emission of radiation from the hot end will be greater than that from the cold end.

Another effect of the recoil of the emission of light may, perhaps, be of

importance in solar physics. Poynting shows that the impulse of solar radiation at the earth is 5.8×10^{-6} dyne per square centimetre. Now the earth is distant 214.4 solar radii from the sun; hence the recoil of light at the sun's surface must be $5.8 \times 10^{-6} \times (214.4)^2 = 2\frac{2}{3}$ dynes per square centimetre. An "atmosphere" is about 10^6 dynes per square centimetre, and although the pressure just computed is very small compared with a terrestrial standard atmosphere, yet its effect may be worthy of consideration.

In the last section the resistance is evaluated which an isolated sphere suffers when moving with uniform velocity in a Lesagian gravific medium. It appears that the resistance is equal to the area of surface of the sphere multiplied by the pressure per unit area on a surface at rest, and by the ratio of the velocity of the sphere to the velocity of the gravific corpuscles. I take it that the same result will give the resistance to motion of a radiating sphere.

On the Phosphorescent Spectra of Sδ and Europium.

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

(Received May 16,—Read June 8, 1905.)

The recent examination of a pure specimen of europium prepared by M. Urbain has brought to light some interesting facts connected with its phosphorescent spectrum when the sulphate is subjected to cathode radiations in a radiant matter tube.

In Demarçay's paper announcing the discovery of europium,* he referred to the phosphorescent spectrum of the new earth in the following terms:—

"In 1885 Sir William Crookes, during his beautiful researches on electric phosphorescence *in vacuo*, noticed a band which he attributed to samarium, and which, by reason of its disappearance in the presence of lime and from certain other peculiarities, he called the 'anomalous line.' Later he distinguished this, together with a large number of other bands, as belonging each to a special meta-element. The hypothetical meta-element corresponding to the anomalous line he called Sδ. M. Lecoq de Boisbaudran, in the course of his important researches on phosphorescence, confirmed the above statements with regard to this anomalous line. In 1892 M. de Boisbaudran described a spectrum consisting of three brilliant blue lines discovered in the spark spectrum of samarium. He concluded that they corresponded to a particular element, Zε. About the same time he also drew attention to a particular band in the reversal spectrum of samarium, which apparently corresponded to the anomalous line. M. de Boisbaudran, without forming very precise conclusions, inclined to the idea that this line was due to a particular element, Zζ. In 1896 I discovered the presence of an element intermediate between gadolinium and samarium. In 1900 I showed that this new element was identical with de Boisbaudran's Zε, and that Crookes's anomalous band was due to the same substance, as well as the reversal line Zζ. . . . Since that period, by a long series of fractionations with magnesium nitrate, I have been able to accumulate a considerable quantity of this element. The apparently contradictory results of Crookes and de Boisbaudran are due, I think, to the very small proportions of Z—Zε contained in their material. I propose the name Europium for the new element, with symbol Eu, and atomic weight 151 (approx.)"

Immediately on the publication of Demarçay's paper I gave reasons why

* 'Comptes Rendus,' vol. 132, p. 1484; 'Chemical News,' vol. 84, p. 1.

my earth giving the very sharp red phosphorescent line (which I had called "the anomalous line"), was not the same as either de Boisbaudran's or Demarçay's earth. I said* "It is necessary for me to make one or two corrections to the paper of M. Demarçay.

"I have never admitted that the body called by M. de Boisbaudran $Z\epsilon$ is the same body which gives my 'anomalous line.' Indeed, I have good reason to think they are quite different. The line given by M. de Boisbaudran's $Z\epsilon$ is broad and indistinct at the edges, while the 'anomalous line' is absolutely sharp and narrow, like a gas-line. Also their refrangibilities are not identical. The same remarks will apply to the body described by M. Demarçay in his 1900 paper."

The first record of the observation of the so-called anomalous line is in my paper "On Radiant Matter Spectroscopy—Part II, Samarium," read before the Royal Society, June 18, 1885,† which contains an account of the conditions under which this line is obtained, and my reasons for supposing it to be indicative of an elementary substance. In paragraph 146, I said:—

"It was interesting to ascertain what spectrum a mixture of samarium and yttrium would give I next tried a mixture of samaria 80, and yttria 20. The spectrum was identical with the one last observed, with one striking difference—the λ^{-2} 2693 line now shines out with great brilliancy of a fine orange-red colour, as sharp as a gas-line, and so unlike the bands usually met with in the spectra of phosphorescent earths as to suggest the explanation that some other spectrum-forming body was present in the mixture."

Again, in the same paper, paragraph 165, I wrote:—

"The anomalous line λ^{-2} 2693.—On several occasions I have spoken of an orange line, λ^{-2} 2693, which by its brilliancy and sharpness is a prominent object in most of the samarium-yttrium spectra. With samaric sulphate it is exceedingly faint. With samaria containing 5 per cent. of yttria it is very little brighter; and with a mixture of 80 parts samaria and 20 parts yttria it is at its maximum intensity."

The next year I returned to the subject, and in a paper "On some New Elements in Gadolinite and Samarskite, Detected Spectroscopically,"‡ I said that I had since further investigated the occurrence of line λ 6094, "the anomalous line," with the bringing to light of some important new facts. I found that the body giving rise to the line closely followed samarium in my fractionations, and that the presence of yttria was not

* 'Chemical News,' vol. 84, p. 2, July 5, 1901.

† 'Phil. Trans.,' Part II, 1885.

‡ 'Roy. Soc. Proc.,' June 9, 1886, vol. 40, p. 502.

necessary to bring it out, the yttria acting only by deadening the brightness of the other red, green, and orange bands of samaria, while it had little or no action on the anomalous line. Again, I found that the addition of a little lime entirely suppressed line λ 6094, while it brought out the samarium lines with increased vigour. I further found that in samaria prepared from different minerals the line varied greatly in intensity. The earth from samarskite showing it strongly, while samaria from gadolinite showed no trace of line λ 6094. "It follows, therefore, that the body whose phosphorescent spectrum gives line λ 6094 occurs in samarskite but not in gadolinite; thus it cannot be due to samarium, yttrium, or a mixture of these two elements. The only other probable alternative is that the source of this line is a new element."

I said:—"A hitherto unrecognised band in the spectra by absorption or phosphorescence is not of itself definite proof of a new element, but if it is supported by chemical facts, such as I have brought forward, there is sufficient *primâ facie* evidence that a new element is present. Until, however, the new earths are separated in sufficient purity to enable their atomic weights to be approximately determined, and their chemical and physical properties observed, I think it is more prudent to regard them as elements on probation." I, therefore, named the new body *Sd*, the *S* recalling the source, samarskite.

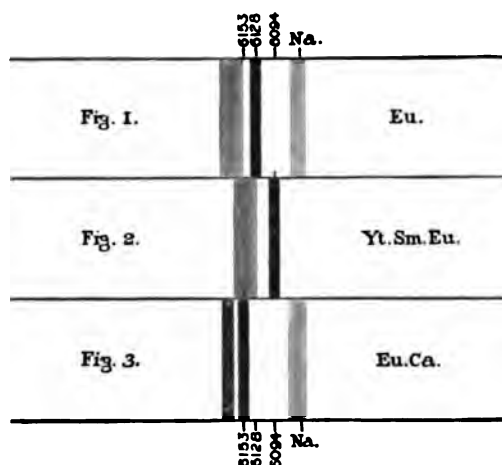
In 1887, I again recurred to the subject of line λ 6094, and in a paper communicated to the Royal Society on February 10, 1887,* I gave the result of an extended search for the earth which gave rise to it, or *Sd*. I said that *Sd* "is not present in the rare earths from gadolinite, xenotime, monazite, hielmite, euxenite, and arrhenite; it is present in small quantity in cerite, and somewhat more plentifully in samarskite. . . . In samarskite yttrium it concentrates at a definite part of the fractionation. A little calcium entirely suppresses the orange line, while samarium or yttrium seem to intensify it."

Owing to want of material and pressure of other occupations, the subject was put aside until recently, when an examination of the phosphorescent spectrum of Urbain's pure europium, in the form of ignited sulphate, led me to take up the matter once more.

Europium sulphate phosphoresces red, as described by Demarçay. A photograph showed a complete absence of phosphorescence bands between λ 4800 and λ 2536. The visible spectrum consists almost exclusively of two red lines, the most refrangible being nebulous and faint, the other sharper and very bright (fig. 1), and a faint nebulosity in the position of the sodium line.

* 'Roy. Soc. Proc.,' vol. 42, p. 112.

The strong phosphorescent line, which Demarçay thinks is identical with my Sδ, is shown by europia and gadolinia; indeed, it is stronger in gadolinia



than in europia. Careful measurement shows it is not coincident with the old anomalous line, the wave-length of the europia line being λ 6128 and that of Sδ λ 6094.

Experiments were made in connection with the appearance of Sδ and the identity or non-identity of it with the similar looking line in Urbain's earths. Some good yttria was mixed with pure samaria in the proportion originally found to give the Sδ line most brilliantly, but the phosphorescing sulphate failed to show any trace of it. To this mixture was now added a little europia, and the Sδ line was developed brilliantly, and occupied its normal position at λ 6094 (fig. 2), in a different position to the line seen when the europia is not contaminated with Yt and Sm. This result was so unusual that both tubes, one containing europium sulphate, and the other Eu, Yt, and Sm sulphate, were arranged so that their two spectra overlapped, when the difference in position was very marked.

It having been found that the addition of lime caused the anomalous line to disappear, it was decided to add lime to pure europia to ascertain its effect. It did not suppress the Eu line, but caused it to shift towards the red to λ 6153, still further away from the position it occupied in mixtures of Yt, Sm, and Eu; and its less refrangible companion, shown faint in figs. 1 and 2, increased to almost equal intensity (fig. 3).

Records of Difference of Temperature between McGill College Observatory, and the Top of Mount Royal, Montreal.

By Professor C. McLEOD, F.R.S.Can.

(Communicated by Professor H. L. Callendar, F.R.S. Received June 7,—Read June 8, 1905.)

A grant of £50 was voted by the British Association in 1897 for erecting a line on Mount Royal to connect the summit with the McGill College Observatory, in order to obtain continuous electrical records in the Observatory with one of Professor Callendar's instruments of the variations of temperature on the summit of Mount Royal at a distance of about a mile, in a situation which was inaccessible for the greater part of the winter. An air-line was erected early in 1898, as soon as the weather permitted, and the thermometers and other instruments adjusted and tested by Professor Callendar. The apparatus worked very well in fine weather, but the insulation was appreciably imperfect during rain. During the summer the original thermometers and part of the line were damaged by lightning, and it was found to be necessary to replace the air-line by a lead-covered cable to secure perfect insulation and protection. The necessary funds for this purpose were provided partly by a grant of £20 from the British Association and partly by a gift of \$300 from Sir Wm. McDonald. The cable was erected in the summer of 1903, and the thermometers refitted.

The cable consisted of four No. 16 copper wires insulated with paper in a thick lead sheath suspended from a steel cable on poles. The length of the cable was 4100 feet, the horizontal distance between the stations 3300 feet, and the difference of altitude, 620 feet. The total resistance of the thermometer leads was about 40 ohms, and was very nearly equal to that of the compensating leads. The resistances were equalised by a short coil of copper wire, placed outside near the observatory. The insulation of the line was tested and found to be ample for the purpose even in wet weather.

In order to secure an open scale for the record, and to obtain the greatest possible accuracy in the measurement of the difference of temperature between the two stations, a pair of similar platinum thermometers, each having a resistance of 9.264 ohms at 32° F., and giving a scale of 1/5 of an inch, or 1/50 of an ohm per degree Fahr., on the recorder, were connected differentially to the recorder, one thermometer being placed in a screen on the top of the mountain at one end of the line, and the other in a similar screen at the other

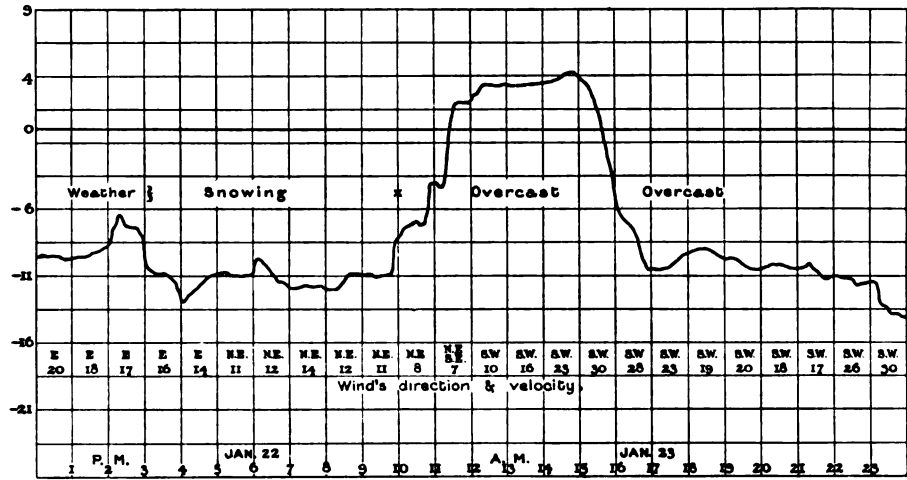
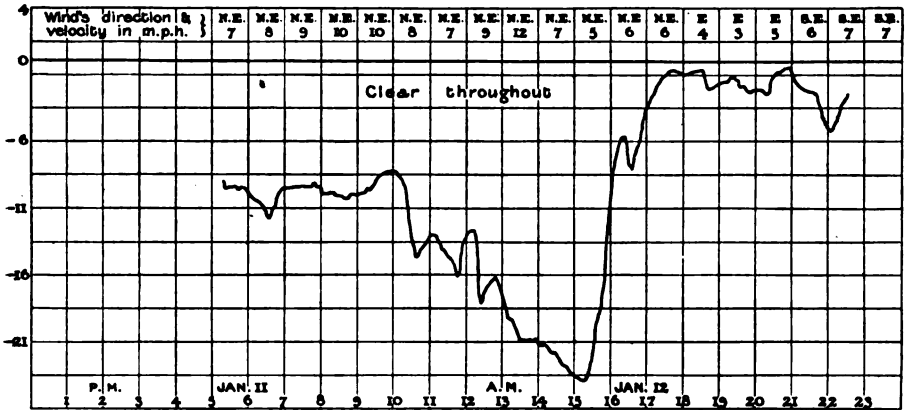
end of the line near the observatory. The position of the zero and the accuracy of compensation of the leads were tested on two occasions at an interval of three months, with satisfactory results. The maximum error due to defective insulation or compensation or variation of zero did not exceed $0^{\circ}5$ F.

The results of the first year's working demonstrate the possibility of obtaining accurate continuous records of the temperature of an inaccessible station without any trouble over long periods. It has not yet been possible to trace the connection between weather conditions and the variations of the difference of temperature between the stations, but some general results of interest appear to be worth noting. The range of variation is considerable, and often changes very rapidly. On some occasions the temperature at the higher station has been as much as 6° or 7° F. above the lower, on others it has been 25° F. below, showing a range of more than 30° F. Normal differences of temperature appear to vary with the average air temperature, increasing negatively (higher station colder) as the temperature falls. This is illustrated by the accompanying table of monthly means. The average difference of temperature varies from $11^{\circ}5$ F. in January, at $8^{\circ}2$ F., to $3^{\circ}7$ F. in May at $59^{\circ}7$ F.

Month.	Mean temperature at lower station.	Higher station colder by—
1903, July.....	$67^{\circ}7$	$5^{\circ}5$
August	$62^{\circ}0$	$4^{\circ}8$
Sept.	$60^{\circ}0$	$5^{\circ}9$
Oct.	$48^{\circ}6$	$7^{\circ}6$
Nov.....	$32^{\circ}1$	$4^{\circ}6$
Dec.....	$14^{\circ}0$	$8^{\circ}3$
1904, Jan.	$8^{\circ}2$	$11^{\circ}5$
Feb.....	$7^{\circ}2$	$8^{\circ}1$
March	$24^{\circ}8$	$5^{\circ}9$
April	$39^{\circ}3$	$6^{\circ}8$
May.....	$59^{\circ}7$	$3^{\circ}7$

As illustrating the general character of the differential records, and the extent and suddenness of the changes observed, three of the records are reproduced on a reduced scale, for January 11, January 22, and February 1, 1904. A complete set of records for February, 1904, which are not reproduced, but preserved for reference in the Archives, also accompanies the paper.

If the differential records are compared with temperature at the lower station, it is at once noticed that any marked change of temperature at the lower station is almost invariably preceded by a similar change at



the higher station at an interval of time from 12 to 24 hours. A negative increase in the temperature difference as shown by the curve on February 1 heralds the arrival of a cold wave. A rise in the difference curve, or a diminution of the temperature difference, indicates the approach of warmer weather. It seems probable that when these relations have been more completely studied and reduced, they may prove of great assistance in forecasting. The system of recording here adopted can be applied equally well to sunshine, and to other meteorological data, and appears to overcome the difficulty and expense of maintaining a staff of observers at an elevated and often inaccessible station.

The Elastic Properties of Steel at High Temperatures.

By BERTRAM HOPKINSON, M.A., M.I.C.E., Professor of Mechanism and Applied Mechanics in the University of Cambridge, and F. ROGERS, B.A. (Cantab.), M.Sc., M.Eng.

(Communicated by Professor Ewing, F.R.S. Received April 13,—Received in Revised Form June 5,—Read June 8, 1905.)

Hitherto, investigations into the elastic properties of metals have been confined to comparatively low temperatures. Gray, Dunlop, and Blyth have measured the modulus of rigidity and Young's modulus for wires up to temperatures of 100°C. , and found that both these quantities decrease as the temperature rises.* Martens determined the influence of heat on the strength of iron up to temperatures of 600°C. , but his experiments were the ordinary tensile tests carried to rupture, and though he also found a substantial diminution of Young's modulus with rise of temperature, he did not go into the point fully, being mainly concerned with breaking stress and elongation.†

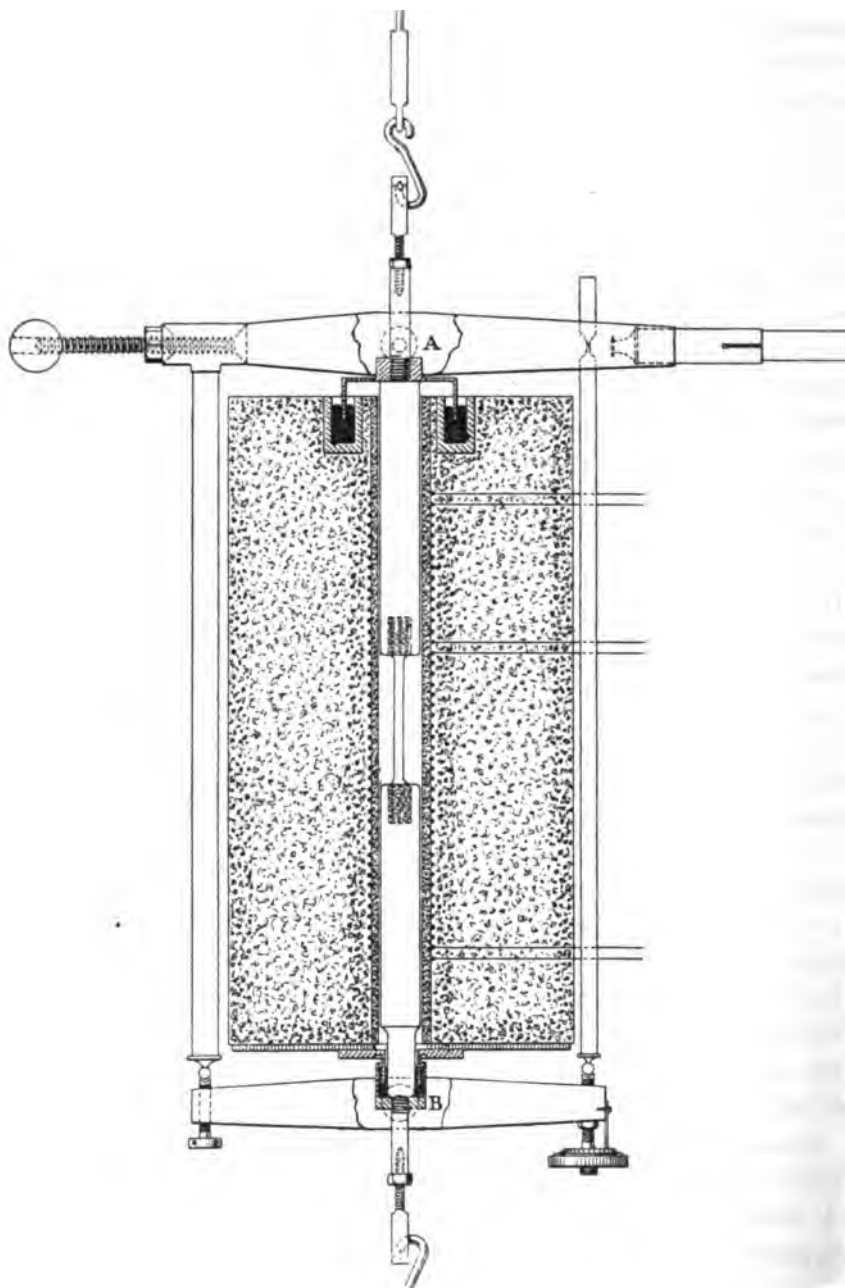
In the experiments here described the elastic properties of steel and iron have been investigated at higher temperatures, ranging up to 800°C. , and for stresses greatly below that required to rupture the material. We have found that as the temperature rises the stress-strain relations undergo a remarkable change, which may best be expressed by saying that what is variously called the "time-effect," or "elastische nachwirkung," or "creeping," increases greatly with the temperature. Steel, at high temperatures, behaves like indiarubber or glass; if it is stressed for a time, and the stress removed, it does not at once recover, but after the immediate elastic recovery there is a slow contraction perceptible for many minutes. Such "creeping" can be detected at ordinary temperatures, but at a red heat it attains a different order of magnitude, becoming (in its total amount) a substantial fraction of the whole deformation.

The test-piece was 4 inches long, about 0.2 inch diameter, and had enlarged ends which were screwed into two steel bars each $1\frac{1}{4}$ inch diameter and 10 inches long. The whole was set up in a vertical electric resistance furnace, wound with three coils of nickel wire. The currents in these coils could be separately controlled, and in this way the temperature along the test-piece could be made very approximately uniform. The temperatures were measured by three thermo couples, placed one at each end and one in the

* 'Proc. Inst. C. E.,' vol. 104, p. 209 (1891).

† 'Roy. Soc. Proc.,' vol. 67, p. 180 (Oct., 1900).

FIG. 1.



middle of the test-piece. Fig. 1 shows the apparatus with one side of the furnace removed. Changes in length between the points A, B could be

measured correctly to $1/50000$ of an inch, by means of an extensometer of Professor Ewing's pattern. The furnace was supported separately, and the test-bar, with the attached extensometer, was hung free within it. Tension up to 112 lbs. ($1\frac{1}{2}$ tons per square inch) could be very rapidly applied or removed by means of a foot lever at the lower end. The interior of the furnace was closed from the atmosphere by means of mercury locks, and the test-piece was kept surrounded by an atmosphere of nitrogen so as to avoid oxidation.

It will be seen that the extension observed included the elongation of the end-pieces, as well as that of the test-piece. The area of the latter being $1/30$ of that of the ends, and its length one-fifth, it appears that of the total extension 87 per cent. is contributed by the test-piece and the remainder by the end-pieces, if the elastic properties of the two are the same. At low temperatures this is approximately the case, but at higher temperatures the average temperature of the ends is less than that of the test-piece, and they, therefore, contribute a less proportion to the total extension. In stating the results in this paper, the total extension is alone referred to, and it is stated in extensometer divisions, each of which is $1/5000$ of an inch, or $1/20000$ of the length of the test-piece. It is probable that at high temperatures over 90 per cent. of this extension should be credited to the test-piece.

Two materials were tested, one being steel containing about 0.5 per cent. of carbon, and the other Low Moor Iron.

Fig. 2 shows the result of a series of tests carried out on a steel bar at 750°C . The bar was at no time heated much beyond that temperature. It was loaded with 85 lbs. for one minute, then unloaded for two minutes and so on, and the curve shows the resulting changes of length in terms of the time. It will be seen that even at this low stress (about $1\frac{1}{2}$ tons per square inch) the metal flows fairly rapidly, and that the overstraining has a considerable hardening effect, as shown by the diminishing amount of the permanent set produced by successive loadings. We found that this hardening disappeared with rest; that is, if the bar were left unstressed at 750°C . for a couple of hours after having been hardened by successive loadings, it was restored to its original soft state. With a slightly less load (about 79 lbs.) the flow of metal was very much slower, the permanent set produced by load applied for one minute amounting to only about 0.5 extensometer division, against 1.5 divisions for the load of 85 lbs.

In respect of all the features hitherto mentioned the properties of the material differ only quantitatively from those of the cold bar. Fig. 2 might, but for one remarkable difference, apply to a cold bar stressed to its yield-point. The difference lies in the behaviour of the bar after the removal of the load. The cold bar does not contract appreciably; there is the instan-

taneous elastic contraction, then it stops.* The hot bar, on the other hand, goes on shortening for two minutes or more after the load is off, as shown by the dotted line on the diagram, and the total amount of such shortening amounts to roughly one-third of the instantaneous contraction, or one-quarter

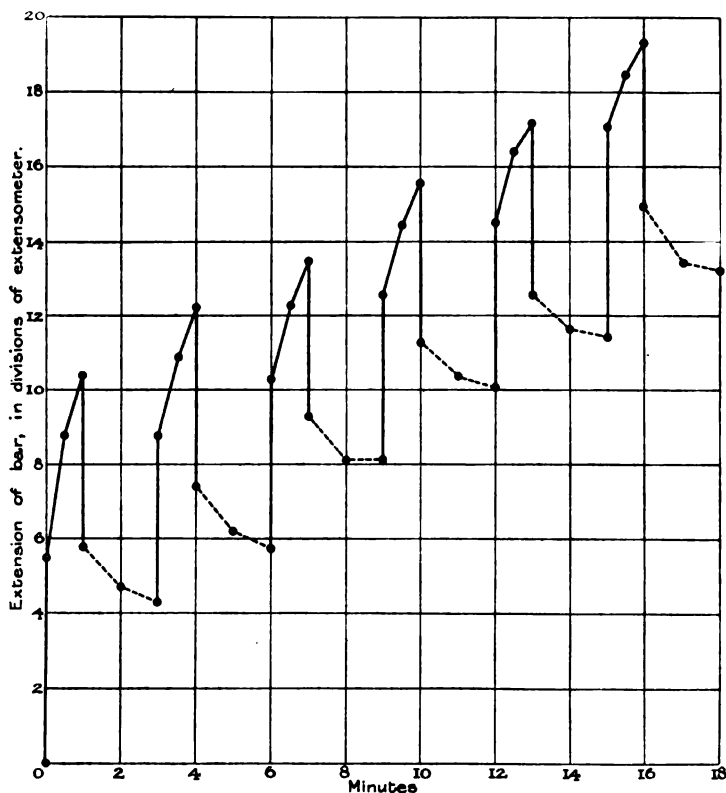


FIG. 2.—Temperature of bar, 750°. Load, 85 lbs. 1 division of extensometer = $\frac{1}{5000}$ " = $\frac{1}{20000}$ part of length of test-piece. During the times covered by the dotted lines the bar was unstressed.

of the total contraction, or one-fifth of the average total extension after hardening has taken effect.

The iron bar behaved in much the same way, but the metal flowed at a lower stress. There was considerable flow with a stress of but half a ton per square inch. The shortening after removal of load was also perceptible at that stress.

* Professor Ewing, 'Roy. Soc. Proc.' vol. 58, p. 123, found a certain amount of creeping after the removal of the load from a cold bar which had previously been stressed beyond its yield-point; but the effect was extremely small, the total creep never amounting to more than one-seventieth of the total extension of the bar when loaded. In a bar which had not previously been overstrained no such effect was observed.

At 600° C. both bars exhibited greater tenacity. A load of 112 lbs. (1·6 tons per square inch) applied to the steel bar for one minute produced an immediate extension of 3·8 divisions, followed by a slow drawing out, which amounted in one minute to about 0·9 division. On removal of load there was an immediate shortening of 3·8 divisions, followed by a slow contraction amounting in two minutes to 0·7 division. The permanent extension produced was very small, if, indeed, there was any at all. The iron bar behaved in a similar way, but as at 750° C. it yielded appreciably at a stress which was not sufficient to permanently deform the steel bar.

The experiment on the steel bar at 600° shows pretty conclusively that this slow recovery after release from stress is not solely, or even mainly, dependent on overstrain. It seems to exist to a large amount with stresses which leave practically no permanent effect; the strain develops slowly under application of stress and disappears slowly after it is removed.

This phenomenon is, of course, analogous to residual charge in glass and other dielectrics; the stress corresponding to the electric force, and the strain to the electric displacement. Whether the law of linear superposition of the effects of stresses—closely followed in the electrical analogy—is true for hot steel or iron, is an interesting question which our apparatus was hardly sufficiently delicate to answer.

The magnitude of this effect in steel may best be gauged by comparing it with other cases of the same kind, *e.g.*, with the slow recovery of a glass fibre after twisting; if such a fibre be twisted through a considerable angle for several hours, it will recover all but one-fiftieth of the twist within two or three seconds of the removal of the stress.* The remaining slow “creep,” amounting to one-fiftieth of the whole deformation, corresponds to the slow return of the steel. In indiarubber, under certain circumstances, 10 per cent. of the strain disappears in time after the removal of the stress.† But in steel, at 600° C., the proportion is about 15 per cent.

The apparatus used was not entirely satisfactory, having been designed for the purpose of measuring larger strains than have been dealt with in this paper. The principal difficulty lay in the slow variations of temperature in the bar and end pieces, which could not be completely controlled, and which produced changes of length masking to some extent the changes due to stress, especially when the latter were spread over considerable times. We cannot do more at this stage, therefore, than assert the existence of a large time-lag between the stress and the strain in steel and iron at temperatures of 600° C. and over; and the figures which we have given must be taken as indications of its order of magnitude only.

* Dr. J. Hopkinson, ‘Original Papers,’ vol. 2, p. 350.

† Phillips, ‘Phil. Mag.,’ April, 1905, p. 513.

One effect of such a time-lag will be to cause dissipation of energy if the material be subjected to alternating stress, for it will lead to a difference of phase between the stress and the strain; and the amount of the dissipation will depend on the period of the oscillations.

Gray, Dunlop and Blythe found an increase in the rate of decay of the torsional oscillations of an iron wire as its temperature was increased to 100°C . On the other hand, Horton* has found a decrease in the rate of decay under circumstances which were apparently the same, except that the period of the oscillations was very much less than in Gray's experiments. These results might be reconciled and explained by the existence of such a time-lag as we have observed at higher temperatures. With our apparatus we could detect no time-lag at temperatures lower than 400°C .; but it is quite possible that it exists to the small extent necessary to account for the decay of oscillations.

Young's Modulus.

Another effect of "creeping," such as we have observed, is to make the determination of Young's modulus a matter of some uncertainty. Thus the extension of the bar at 600°C . produced by a given load varies 15 per cent. or more, according to the time of application of the load. When, however, the load is applied for a very short time, say of the order of one or two seconds, the strain produced seems to approach to a definite limiting value, which is the instantaneous extension or contraction of the bar observed in our experiments when the load is applied or removed. It seems reasonable to define Young's modulus for a metal in this state, as the stress divided by this limiting instantaneous strain. It is then independent of the manner of loading, and is a definite physical constant; otherwise not. We have shown in Fig. 3 the relation between Young's modulus, so defined, and the temperature. The ordinate is the reciprocal of the instantaneous extension produced by the load of 112 lbs. Owing to the effect of the ends, the reciprocal of the extension is not quite proportional to Young's modulus, their ratio being somewhat greater at high temperatures than at low, as already explained. With regard to this Fig. it should be noted that the error in the determinations on the cold bar and at 400°C . is probably not more than about 2 per cent. At higher temperatures the error is greater, as, owing to the rapid drawing out of the bar, it was difficult to be sure of the instantaneous extension. It is, however, fairly certain that the ratio of Young's modulus in the cold bar and at 750°C . (as shown by the point D') is not more than 10 per cent. in error. The points were observed in alphabetical order, and it was

* 'Phil. Trans.,' A, vol. 204, p. 1.

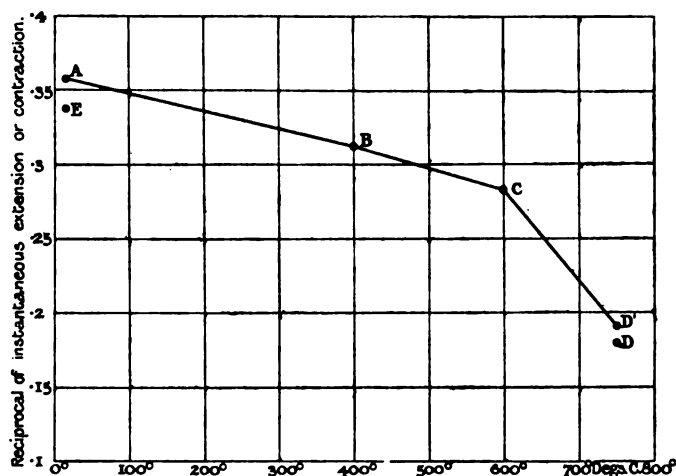


FIG. 3.—Variation of Young's modulus with temperature. Load, 112 lbs.

found that, in spite of our efforts to secure a neutral atmosphere, the bar had scaled somewhat after heating to 750°C . This accounts for the larger extension shown by the point E, which was taken in the cold, after heating. After taking this point the bar was taken out, cleaned and gauged, when its area was found to be reduced by about 6 per cent. Allowing for the reduced area, the points E and A are in good agreement; but, of course, there is some little uncertainty from this cause as to the position of the point D. If the full reduction of 6 per cent. in the area be allowed for, the corrected position is at D', and this is probably not far from the truth.

In the iron bar the change of Young's modulus with temperature was of the same character but greater. The value in the cold being taken as unity, that at 600°C . was about 0.6, while at 750° it was about 0.5.

On the Refractive Index of Gaseous Fluorine.

By C. CUTHBERTSON and E. B. R. PRIDEAUX, M.A., B.Sc.

(Communicated by Sir William Ramsay, K.C.B., F.R.S. Received June 5,—
Read June 8, 1905.)

(Abstract.)

The authors have determined the refractive index of gaseous fluorine for sodium light by means of Jamin's refractometer. Five experiments gave values for the refractivity $(\mu-1)10^6$ of 195, 177, 192, 194 and 198½. The discrepancy exhibited by the second experiment can be accounted for, and it is believed that the mean of the other four experiments, 195, is within 2 or 3 per cent. of the true value.

The gas was prepared in a copper electrolytic tube, similar to that used by M. Moissan, and, after being purified from the vapour of hydrofluoric acid and from ozone, was made to displace dry air from a refractometer tube of platinum-iridium, whose ends were closed by plates of fluorspar. It was found by experience that it was impossible to obtain the gas completely free from air, or oxygen, produced during electrolysis, and it was necessary, therefore, to analyse the mixture of gases contained in the refractometer tube at the moment when the index was observed.

The method employed for this purpose was to bring the gases into contact with dry lead filings in a closed space, and to estimate the volume of fluorine from the contraction. When the refractometer tube was filled with the gases produced by electrolysis, it was disconnected from the source of supply and its exit and entry tubes rapidly connected with two closed burettes, half filled with mercury, having at their upper extremities a narrow tube containing a large quantity of dry lead filings. Each closed burette was in communication with an open tube, and one was also connected with a reservoir of mercury. The open tubes were connected by a wire passing over a pulley, so that when one was raised the other fell by an equal height. By moving these tubes the mixture of gases in the refractometer tube was pushed into the tube containing the lead filings, where the fluorine was absorbed as lead fluoride. As contraction occurred, the pressure was equalised by letting in mercury from the reservoir, and in this manner the quantity of fluorine present was measured. The oxygen contained in the residual gases was measured by burning with phosphorus, and the remainder was found to be nitrogen.

Throughout the experiments it was observed that the amount of oxygen present in the current of gases proceeding from the electrolytic tube was

always in excess of that due to the air present. After prolonged investigation it was ascertained that this oxygen was not formed by the action of fluorine on moisture in the train of purifiers, but was produced by electrolysis, probably from water absorbed by the solution. Contrary to expectation, this water was not electrolysed away before the fluorine appeared, but persisted throughout the experiment, perhaps owing to the gradual melting of a crystalline solid in the electrolytic tube.

In a recent paper,* one of the authors has attempted to show that the refractivities of the different members of the same chemical group are related in the ratios of small integers; and it was observed that, if this coincidence were not due to chance, the refractivity of fluorine should bear to that of chlorine the ratio of 1 to 4, which those of neon, oxygen and nitrogen bear to argon, sulphur and phosphorus respectively. This prediction has been verified. The refractivity of chlorine for sodium light is 768, or 192×4 ; and that now found for fluorine is 195, a discrepancy of $1\frac{1}{2}$ per cent., which is well within the limits of error of the experiment.

* 'Phil. Trans.,' A, vol. 204, p. 323, 1905.

The Absorption Spectrum and Fluorescence of Mercury Vapour.

By W. N. HARTLEY, D.Sc., F.R.S.

(Received June 16, 1905.)

Having undertaken the investigation of the absorption spectra of metals in a state of vapour, the first substance examined was mercury, and as the results are interesting I have deemed it advisable to make them a separate communication to the Society. F. P. le Roux describes the vapour of mercury as having a bluish colour,* and according to R. J. Strutt, it transmits a feeble steel-blue colour, but the absorption coefficient is small.†

Experimental.—The substance to be volatilised was contained in a flask of Heraeus' quartz-glass, with a side tube to the neck from which the metal may be distilled and condensed. To the side tube a water-jacket is fitted through which a constant stream of water may be passed if necessary. The rays from the condensed spark of a pair of lead-cadmium and tin-cadmium electrodes were passed through the flask and on to a cylindrical condensing lens of quartz which focussed the rays on to the slit of a quartz spectrograph.

The mercury to be used was first purified by distillation. The photographic plates used were various, such as "Rainbow Fast" Warwick plates, Lumière isochromatic, yellow-green sensitive, and Cadett and Neall's "Lightning Spectrum" plates. The mercury vapour in the flask was at a pressure of 847 mm., the barometer standing at 763 mm., but the vapour was under a pressure of a column of 84 mm. of mercury above that of the atmosphere. The temperature was about 360° C., the b.p. at 760 mm. being 357°. The volume of the vapour was 31 c.c., and its weight was calculated to be 0.133 gramme. The thickness of the layer of vapour was 37 mm.

Several photographs were taken, and particular care was exercised so as to have both ends of the spectrum, as well as the central part, in accurate focus. The developer used was "imogen sulphite."

The Absorption Spectrum.—The whole rays were transmitted from the red to a point in the ultra-violet where there is a tin line at λ 2571.67. From there to λ 2526.8 there is a very sharply defined and intense absorption band, somewhat degraded on the side towards the red; beyond that the rays are transmitted with full intensity to a wave-length about 2000.

The Fluorescence.—When the mercury was boiling briskly the whole side of the flask nearest to the spark was lighted up with a green fluorescence;

* 'Comptes Rendus,' vol. 51, p. 171, 1860.

† 'Phil. Mag.' (6), vol. 4, p. 596, 1902, and vol. 6, p. 76, 1903.

this penetrated about one-third of the space within the flask, and lighted up the interior. The quartz-glass itself was not fluorescent in the slightest degree.

When all the liquid mercury had become converted into vapour, the temperature no doubt rose above that of the boiling mercury, the vapour was quiescent, and the fluorescence ceased. The interior of the flask was then quite dark. By shaking some of the condensed cold mercury down into the flask the fluorescence was resumed directly the liquid boiled again, but the dropping of cold mercury into the heated vapour caused condensation, and only after the flask had again become filled with the mercury vapour was the fluorescence fully displayed.

When the vapour was rising from the boiling globule of mercury after the cold metal had condensed all within the flask, the vapour could be seen by its fluorescence to undergo condensation in the upper part of the vessel and descend to the hotter space below.

It occurred to me that the actual fluorescence might be associated with oxidation of the vapour, and that it appeared only when such chemical action was taking place, but subsequent observations showed that this could not be the case, because the temperature was above that when oxidation could occur at the time when the fluorescence was most brilliant, and when it most completely filled the vessel, and also when the mercury vapour had expelled all the air. When the temperature rose above the boiling point of mercury and excess of liquid mercury and vapour had been expelled from the flask the fluorescence ceased.

This fact leads to the inference that the fluorescence occurs only between a lower and a higher limit of temperature. What these small differences really are I had no means of determining. Having established the fact that the property of selective absorption is possessed by small quantities of mercury vapour, it was resolved to ascertain whether the band showed itself in solutions of mercury compounds. As a rule the absorption spectra of compounds differ from those of the elements entering into their composition entirely, as in the case of the halogen compounds of the alkali metals; sometimes it is a question of degree, as in the case of the compounds of the rare earth metals, in which similar bands are observed in different salts of the same metal, but in different positions, which vary with the molecular weight of the salts; and there are, still further, other instances where the absorption bands of the solutions are distinctly the properties of the salts, as in the case of the chlorides, bromides, and iodides of cobalt. The salt chosen for examination, because it is the most definite and most soluble, was mercuric chloride. It was examined in cells of 40 mm. thick, diminishing to 1 mm. in thickness.

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The solution contained in the same volume ten times as much mercury as the vapour which filled the flask, or 1·8 gramme of mercuric chloride in 31 c.c. of water; more dilute solutions were examined containing 0·18 gramme and 0·018 gramme. No absorption band was visible on any of the spectra photographed, but there was a continuous absorption at the more refrangible end of the spectrum, which regularly diminished as the quantity of mercuric chloride in the solution decreased.

Further details are as follows :—

1·8 grammes of mercuric chloride in a cell 40 mm. thick transmitted all rays to λ 2702, in 1 mm. to λ 2572; 0·18 gramme in a cell 2 mm. thick transmitted all rays to λ 2265; and 0·018 gramme in similar circumstances transmitted very feebly to λ 2145.

The absorption band in the vapour of mercury belongs to the vapour, and is accompanied by strong fluorescence between a certain maximum and minimum of temperature lying very near to the boiling point.

In studying the fluorescence of solutions of organic compounds I have shown that it is necessary to use the ultra-violet rays and quartz apparatus,* as it was found that fluorescence was associated very generally with a powerful absorption of rays in the ultra-violet. It is a question still undecided whether the rays absorbed by mercury vapour as shown by the band I have measured, reappear with a lowered refrangibility as yellowish-green light in accordance with the law of Stokes.

The spectra were photographed with all due care by my assistant, Mr. Douglass Mellon, A.R.C.Sc.I.

* "Observations on the Origin of Colour and Fluorescence," 'Chem. Soc. Trans.,' vol. 63, pp. 245—256, 1893.

The Formation of Ice and the Grained Structure of Glaciers.

By G. QUINCKE, For. Mem. R.S., Professor of Physics in the University of Heidelberg.

(Received June 19, 1905.)

In the following pages I have the honour to lay before the Royal Society the results of a lengthy research on the formation of ice and the grained structure of glaciers, which may serve as a complement to the previous investigations on the same subject published in the 'Philosophical Transactions' and 'Proceedings of the Royal Society' by Forbes, Tyndall and Huxley, Tyndall, Faraday, T. Graham, J. F. Main, J. C. McConnel and D. A. Kidd, and elsewhere by Guyot, Agassiz, James Thomson, and Sir William Thomson (now Lord Kelvin), Hermann and Adolf Schlagintweit, Person, Leydolt, Rüdorff, Bertin, Grad and A. Dupré, Moseley, A. Heim, J. T. Bottomley, K. R. Koch and Klocke, Forel, Ed. Hagenbach-Bischoff, E. von Drygalski, Mügge, H. Hess and others.

1. It will be convenient at the outset to define the precise meaning with which it is proposed to employ certain words, some of which are in vague popular use, while others are less familiar or new.

By an *oily* liquid will be meant one which has surface tension in the common surface with other liquids with which it may be in contact. According to this definition a solution of any salt will, in comparison with pure water or a weaker salt solution, be called, under certain circumstances, an oily liquid.

An *emulsion* is a watery liquid containing suspended drops of oily liquid, or drops of any sort enclosed in an oily skin. These drops can coalesce into larger drops, or the oily skins can join on to one another, and form a continuous mass of bubbles or foam. Thus *foam* consists of portions of watery liquid enclosed in, and separated from, one another by adjacent partitions of oily liquid. Each space thus enclosed will be called a *foam-cell*, and the enclosing partition the *foam-wall*. If the foam-cells are very small, and the fluid foam-walls very thin (or invisible), the whole is then a *liquid jelly*. The jelly is stiff, the foam stiff or solid, when the walls or the contents of the foam-cells, or both, have become solid.

"*Nearly pure*" applied to water or ice will be used in the special sense of "containing only very small amounts of any salt." *Salt* itself is used throughout in the general chemical sense, that is, not restricted to sodium chloride.

2. I have allowed pure water, and water containing dissolved salt, to freeze in the dark at various rates, and to melt away slowly in the dark, in open air, and in sunlight. The ice prisms employed were from 1 to 1000 mm. thick, and as the thawing proceeded their various layers were systematically examined—sometimes for days together—with the naked eye, with the microscope, and with polarized light. The same appearances presented themselves in the same order as those which for 37 years past I have investigated and described in solutions of silicic acid, glue, or other colloids, when these are evaporated to form gelatinous masses or thin films, and develop fissures. I have shown that thin viscous oily films of more concentrated solution exist in a less concentrated solution of the same substance, and form folds, straight and twisted tubes, cylinders or cones, spheres and bubbles, open and closed foam-cells with visible and invisible foam walls. Thin solid films behave like films of very viscous liquid. Whether the oily films form tubes or bubbles and foam-cells joining on to one another, depends on the viscosity of the oily liquid. The mutual inclination of the foam walls, and their surface tensions, continually change as the concentration of the oily liquid changes, and in the case of invisible foam-walls may depend also on the thickness of the oily film. When the oily film is very thin, its surface tension diminishes with diminishing thickness of the film. Oily foam-walls that are formed against solid surfaces are normal to these surfaces. If three oily foam-walls meet in a common edge at equal angles of 120° they have equal surface tensions.

The foam-cells of a liquid jelly immersed in water can increase or diminish in volume by the diffusion of water through the foam-wall inwards or outwards, *i.e.*, the liquid jelly can *swell* or *shrink*. Two clots of liquid jelly can coalesce into one, which does not occur with clots of solid jelly, nor can these latter swell or shrink.

A liquid jelly becomes for the time being positively or negatively doubly refracting when the viscous walls, or the viscous contents of the foam-cells, are expanded or compressed. A jelly remains permanently doubly refracting when the walls or the contents of the foam-chambers solidify while in an expanded condition.

3. Now, ice is a liquid jelly, with foam-walls of concentrated “oily” salt solution, which enclose foam-cells containing viscous, doubly refracting, pure or nearly pure water.

4. The further the temperature falls below 0° , the greater is the viscosity of both liquids—in the walls and in the interior of the foam-cells—and the less the plasticity of the ice.

5. At very low temperatures the ice breaks with conchoidal fracture

at the surface of the invisible spherical foam-walls, which as the whole cools have contracted differently from their contents.

6. The "glacier grains" are foam-cells filled with pure or nearly pure ice, and separated from one another by visible or invisible walls of oily salt solution.

7. The union of two pieces of ice under water ("Regelation"), and the increase in size of the glacier grains as they approach the lower end of the glacier, correspond to the running together of two gelatinous clots (of silicic acid, or glue) containing liquid foam-cells and liquid cell-contents. At the same time the oily foam-walls between the glacier grains become thicker, and then get thinner again through the draining away of the liquid salt solution at the foot of the glacier.

8. All water, even the purest, contains traces of salt. As the water cools, ice crystals and oily mother liquor separate at short intervals, or periodically. Under the influence of the surface tension, the oily salt solution forms invisible foam-walls, whose surface tension decreases as the thickness of the walls and the concentration of the salt solution diminish. Otherwise, as the cooling proceeds, the salt solution becomes continually more concentrated, and the wall thinner. Finally, the concentrated salt solution also freezes to ice and solid salt. The value of the surface tension determines the angles at which three walls meet in a common edge. If three foam-walls meet at equal angles of 120° , the three walls have equal surface tensions, whereas an inclination of 90° means that fluid foam-walls have been formed in contact with old and already solidified ones.

9. When water containing air freezes, the air, like the salts dissolved in the water, separates out at short intervals, or periodically. The white places in ice, which are those containing these air bubbles, are also the richest in salt.

10. As water containing salt, but free from air, cools, the periodical separation of ice and salt gives rise, alike in sea ice, in artificial ice, and in glacier ice, to layers of ice containing varying amounts of salt. By pressure or by absorption of radiation (sunlight, electric light, or daylight), the parts of the ice which are rich in salt melt sooner than pure ice.

11. In sunlight or electric light furrows are formed at the places rich in salt on the surface of sea ice, artificial ice, and glacier ice. (Forel's stripes; Forbes' "dirt bands"; foam-walls of the great foam-cells of the Kjendal Glacier.)

12. The salt solution formed in sea ice, artificial ice, or glacier ice, through pressure or sunshine, shows, by the hollows which it fills, the forms assumed under the influence of the surface tension by the boundary between the oily

salt solution and the water just before the freezing of the water. As the ice melts, it contracts. Thus in sea ice pressure or absorption of heat radiation causes the formation, in horizontal layers parallel to the frozen surface, of Tyndall's liquefaction figures, vacuous bubbles, ice flowers, and "fir trees" with branches meeting at 120° and 90° , just like those obtained when colloid solutions are evaporated to dryness, or when salt solutions are allowed to crystallise.

In the case of artificial ice which has been frozen in deep prismatic troughs, these liquefaction figures are formed in the diagonal and median planes of the ice block, which were the last parts to freeze, and where the mother liquor had accumulated.

13. Sea ice and artificial ice break up in sunlight into little hexagonal prisms of clear ice. These suffer mutual displacement the less easily the thinner are the fine foam-walls (which have now melted again, and which, when the freezing took place, were formed out of oily salt solution, normal to the surface) and the less salt the water contained before freezing.

The purer the water was, the larger are these hexagonal prisms or foam-cells.

14. The capillary fissures in transparent glacier ice are these fine foam-walls of oily salt solution.

15. When water containing little salt freezes in deep metal troughs surrounded with strongly-cooled brine, the oily salt solution separates in thin layers normal to the surface, and forms bubbles, foam-cells clinging to one another, or—when the oily liquid at low temperatures is very viscous—folds or hollow pipes, which are filled with pure or nearly pure ice, or with air if such were present in the water. The artificial ice is seen to be traversed by many horizontal tubes, normal to the surface, which are specially numerous in the diagonal and median planes of the ice block, where the mother liquor had accumulated. The less salt is contained in the ice, the more transparent are these diagonal and median planes of the artificial ice block.

Illumination with sunlight or daylight causes the appearance of fresh tubes. The ice becomes more cloudy, and subsequently more transparent again.

16. When water containing air freezes in deep metal troughs, the upper part of the ice block shows horizontal layers consisting alternately of transparent pure ice and of opaque salt-containing ice with numerous air bubbles. The more salt the water contains, the more numerous and the closer are the opaque layers. In sunlight these opaque layers melt more easily than the transparent ones, and furrows are formed on the surface of the opaque ice.

17. If the ice is allowed to thaw again in a warm room, or is exposed to

radiation (daylight), the parts rich in salt melt sooner than those which contain little salt. The tubes of oily salt solution bulge and coil up, and then break up with contraction of volume into spherical bubbles, which may be vacuous or filled with air. The foam-cells exhibit the shapes like those of colloids and jellies as they swell or shrink, or those tree-like and branched formations which I have described in the case of the "liquid precipitates" of metallic silicates and cyanides. If the capillary fissures in this opaque ice are filled with very viscous salt solution, or if the oily salt solution forms no continuous foam-cells, it cannot run away. The ice remains white, as glacier ice actually does.

18. When an ice block thaws under the long-continued action of daylight, there appear, in the diagonal and median planes of the block, bright bands and cloudy bands, which change their shape and position as the duration and intensity of the radiation alters. This is due to the formation of new foam-walls of oily salt solution and the disappearance of old ones. The angles between the foam-walls are also seen to change, which means that the surface tension of these walls is changing. Now as the amount of salt in the diagonal planes increases, and the absorbed radiation diminishes, towards the interior of the ice, and as further the surface tension and viscosity alter with changing concentration and temperature, it follows that the shapes assumed by the oily layers in the interior of the ice under the influence of the surface tension also undergo change.

19. After 30 to 36 hours, the block of artificial ice had melted in the warm room to half its original height (1 metre), and at the foot and warmer places had given way in a pasty mass. In the upper portion foam-walls had formed in the pure ice, inclined 120° to one another. In these, as in the median layer that had thawed away, melting salt solution ran down for hours. At the warmer places, and at the thin uppermost crust, glacier grains were formed. These were foam-cells, 5 to 10 mm. wide, filled with doubly refracting ice, and separated from one another by singly refracting foam-walls of transparent salt solution. At the junctions of the foam-walls there often lay tetrahedra, bounded by spherical surfaces and filled with transparent liquid.

20. In the diagonal and median planes of a block of artificial ice (1 metre high) containing a certain very small amount of salt, and exposed to a certain intensity of radiation, there can be formed horizontal closed tubes of pure or nearly pure ice, having rounded heads and sides bulging at places, and filled with liquid salt solution. They slowly swell, slowly break up into separate bubbles, and then slowly pass away. They are first formed low down, at places of high pressure, and afterwards higher up, at places of low pressure.

21. When distilled water, free from air, was frozen in iron troughs, it was

found at a certain temperature or with a certain concentration of the salt solution and the oily foam-wall, that the walls and contents of the closed tubes in the lower part of the median plane were for some time coloured yellow. Subsequently this colour disappeared. It was not present when the water was frozen in brass troughs. I believe it was due to ferric oxide, which was differently soluble in the walls and in the liquid inside the foam-cells, and at a higher temperature became insoluble and sank to the bottom.

22. The phenomena of melting ice depend both on the velocity of freezing and the velocity of thawing. The more rapidly the water freezes, the more numerous are the foam-walls, and the smaller the foam-cells.

23. Very dilute solutions of different salts, when slowly frozen under similar conditions, give oily layers of varying viscosity and surface tension or spheres, bubbles, tubes and foam-walls of varying form. I have shown this with freshly boiled water containing 0.000003 per cent. of NaCl, or equivalent quantities of KCl, K_2CO_3 , Na_2SO_4 , $CaCl_2$, $MgCl_2$, $Al_2(SO_4)_3$. The water was frozen in prismatic troughs of brass or tin.

24. During the freezing of water containing 0.0015 per cent. of Na_2SO_4 , and also containing air, the air separated at the same time as the mother liquor. The bounding surface between air and almost solidified, very viscous liquid, tends to become as small as possible, and rolls up together to form hollow cylinders, whose radii are the smaller the more quickly the ice has frozen. The water freezes the more slowly, the further it is from the strongly cooled (below 0°) side of the trough. The thin layers forming the walls of the tubes are normal to the solid surface of the side of the trough, or of the transparent mantle of ice which encloses the mother liquor. They frequently form cylindrical or conical tubes, 6 to 12 mm. long, with a whitish skin, and filled with air. Their axes are normal to the surface, and their pointed ends are directed towards the outer side of the ice mantle. At the base of the tubes, which may be 0.5 to 2 mm. wide, there hangs a whitish hollow sphere inside the mother liquor.

25. On slowly freezing water containing from 0.00014 to 0.0014 per cent. of Na_2SO_4 or 0.003 per cent. of NaCl, it happens at times that the mother liquor, which is surrounded by a transparent mantle of ice, contains numerous flat crystalline plates of pure ice. These, by their shape, position and inclination to one another, clearly show that they have been formed from thin oily foam-walls of pure water, which, as the cooling proceeded, have separated from the watery salt solution, and then solidified.

26. When a test tube, containing boiling distilled water, is plunged into liquid air, the water freezes very quickly to a milky-white mass of ice, with fissures normal to the surface of the glass. If the test-tube with the white

ice—the whole being now cooled down to -190° —is plunged into distilled water, it becomes coated on the outside with a thin crust of ice, which can be detached with a knife, and examined in a watch glass under the polarising microscope. It consists of small glacier grains or foam-cells (0.1 to 0.2 mm. in diameter) whose flat walls are normal to the cylindrical surface, and are inclined to one another at angles of 120° , 110° and so on. The interior of each foam-cell contains a crystal of ice, which in the different cells is differently orientated. When the ice in the test-tube is crushed with a steel point, it exhibits a fibrous fracture, with fine fibres normal to the cylindrical surface. Occasionally in the cross-section are seen concentric cylinders composed alternately of transparent and of white ice. The latent heat of the slowly freezing water diminishes the loss of heat, and the velocity of cooling changes. The ice in the transparent layers was frozen slowly, that in the opaque ones quickly. As this ice thaws in a watch glass under the polarising microscope, the lumps of quickly-frozen white ice exhibit immense numbers of strings—arranged radially alongside one another—of spheres and lenticular masses, 0.01 to 0.02 mm. in thickness, consisting of very nearly pure water. In each sphere there was a vacuous bubble 0.0006 mm. in diameter.

27. Slowly-frozen water showed, on thawing, similar strings of (liquid) spheres and lenticular masses (of larger size, viz., 0.04 to 0.12 mm. diameter), normal to the surface of the block of ice. These spheres and lens-shaped masses had been formed out of solid or hollow cylinders, or long thin cones with local swellings or bulgings. Frequently lens-shaped masses bounded by two spherical surfaces lay in a thin, flat, spiral or warped foam-wall.

28. The fibres and cylindrical or conical tubes, like the tubes filled with air, are formed out of thin layers of very viscous, oily liquid, which, as the cooling proceeded, separated out, normal to the surface, and under the influence of the surface tension rolled up, being unable, by reason of excessive viscosity, to form spheres or bubbles.

29. When the thawing has gone on for a long time, fewer foam-walls and larger foam-cells, or glacier grains, appear in the lumps of ice. The strings of liquid spheres, normal to the surface, show an increase in the size of the spheres, caused by the coalescence of the small spheres in the doubly-refracting mass of ice into larger ones. An increased amount of salt in the ice assists this coalescence. The tubes or strings of spheres could often be followed continuously through several glacier grains. The partition walls of the glacier grains, when illuminated, often show hundreds of small lens-shaped masses of the same or gradually diminishing size.

30. By repeated fractional freezing and melting of the ice crystals formed, continually purer and purer ice is obtained, with increasingly large foam-

cells or glacier grains. I have, however, not yet succeeded, even by repeated slow freezing, in obtaining ice free from foam-walls or from glacier grains.

31. A block of transparent ice was cut through, as described by Bottomley, with a loaded wire loop. The loop was of steel wire, or of platinum wire previously heated to redness, and carried 2 kilogrammes or more. In no case was the plane of section transparent, but always opaque from the presence of solidified foam bubbles of oily salt solution, possessing refracting power different from that of their surroundings.

32. Each separate glacier grain in artificial ice contains a differently orientated crystal of ice, whose optic axis is very seldom normal to the surface of the ice. When in natural sea ice the optic axes of the separate crystals in the different grains are found to be normal or parallel to the free surface of the water, the separation of orientated crystals of ice may have been started by the contact-action of ice crystals or snow flakes falling on the surface of the super-cooled water, and swimming thereon in a horizontal position.

33. The more slowly artificial ice has frozen, and the less salt it contains, the more transparent, rigid, and difficult to cut with a knife it is.

34. Every block of artificial ice cleaves, on pressure with a steel point, along the diagonal and median planes, in which, as the ice crystals separated out on freezing, the mother liquor became more concentrated through holding the traces of salt dissolved in a continually diminishing volume of liquid.

35. The planes of easiest cleavage in natural ice crystals (laminated structure, displacement without bending) are due to invisible layers of liquid salt solution which are embedded in the crystals, normal to the optic axis, or often in other positions.

36. Ice crystals at temperatures below 0° consist of doubly-refracting viscous liquid, and are intermediate between the soft crystals of serum albumen and ordinary crystals of quartz, felspar, etc.

37. At the edge of Tyndall's liquefaction figures, while they are in process of enlarging, or on the bursting of the foam-walls of artificial ice as it melts, one often sees periodic vortex movements. These arise from a periodic capillary spreading out ("Ausbreitung") of the salt solution of the foam-walls at the boundary between pure water and air or vacuum.

38. Tyndall and Huxley observed in white glacier ice transparent lenticular masses bounded by spherical surfaces. These were foam bubbles of water free from air, which were enclosed in a thin skin of oily salt solution and had solidified while embedded in such a skin.

39. The blue bands in glacier ice consist of pure ice, while the white bands are composed of ice containing salt and air bubbles. They are formed by the periodical action of solar radiation and by changing pressure, or by the slow descent of the portions rich in salt, or by the slow ascent of air bubbles in the viscous liquid of the glacier ice.

40. The ice of the snow flakes which fall on the upper part of the glacier becomes fertilised with inorganic salts derived from disintegrated rocks, and is, as it were, hatched out by the sun's rays, forming "névé" or "firn" snow and glacier grains, or foam-cells filled with ice in the glacier proper. The glacier ice travels on, rolling (or "wallowing") slowly downwards as a living river of ice. Its skeleton of liquid salt solution changes the while, and forms new and larger foam-cells, which, at the lower end of the glacier, perish, disappear, and flow away as the water of the glacier stream.

On the Influence of Collisions and of the Motion of Molecules in the Line of Sight, upon the Constitution of a Spectrum Line.

By LORD RAYLEIGH, O.M., F.R.S.

(Received July 1, 1905.)

Apart from the above and other causes of disturbance, a line in the spectrum of a radiating gas would be infinitely narrow. A good many years ago,* in connection with some estimates by Ebert, I investigated the widening of a line in consequence of the motion of molecules in the line of sight, taking as a basis Maxwell's well-known law respecting the distribution of velocities among colliding molecules, and I calculated the number of interference-bands to be expected, upon a certain supposition as to the degree of contrast between dark and bright parts necessary for visibility. In this investigation no regard was paid to the collisions; the vibrations issuing from each molecule being supposed to be maintained with complete regularity for an indefinite time.

Although little is known with certainty respecting the genesis of radiation, it has long been thought that collisions act as another source of disturbance. The vibrations of a molecule are supposed to remain undisturbed while a free path is described, but to be liable to sudden and arbitrary alteration of phase and amplitude when another molecule is encountered. A limitation in the number of vibrations executed with regularity necessarily implies a certain indeterminateness in the frequency, that is a dilatation of the spectrum line. In its nature this effect is independent of the Doppler effect—for example, it will be diminished relatively to the latter if the molecules are smaller; but the problem naturally arises of calculating the conjoint action of both causes upon the constitution of a spectrum line. This is the question considered by Mr. C. Godfrey in an interesting paper,† upon which it is the principal object of the present note to comment. The formulæ at which he arrives are somewhat complicated, and they are discussed only in the case in which the density of the gas is reduced without limit. According to my view this should cause the influence of the collisions to disappear, so that the results should coincide with those already referred to where the collisions were disregarded from the outset. Nevertheless, the results of the two calculations differ by 10 per cent., that of Mr. Godfrey giving a *narrower* spectrum line than the other.

* 'Phil. Mag.,' vol. 27, p. 298, 1889; 'Scientific Papers,' vol. 3, p. 258.

† "On the Application of Fourier's Double Integrals to Optical Problems, 'Phil. Trans.,' A, vol. 195, p. 329, 1899.

The difference of 10 per cent. is not of much importance in itself, but a discrepancy of this kind involves a subject in a cloud of doubt, which it is desirable, if possible, to dissipate. Mr. Godfrey himself characterises the discrepancy as paradoxical, and advances some considerations towards the elucidation of it. I have a strong feeling, which I think I expressed at the time, that the 10-per-cent. correction is inadmissible, and that there should be no ambiguity or discontinuity in passing to the limit of free paths infinitely long. In connection with some other work I have recently resumed the consideration of the question, and I am disposed to think that Mr. Godfrey's calculation involves an error respecting the way in which the various free paths are averaged.

The first question is as to the character of the spectrum line corresponding to a regular vibration which extends over a *finite* interval of time. As the energy lying between the limits n and $n + dn$ of frequency (or rather inverse wave-length), Mr. Godfrey finds from Fourier's theorem

$$\frac{\sin^2 \pi r n}{n^2} dn, \quad (1)$$

r denoting the finite length of the train of waves, and n being measured from that value which would be dominant if r were infinitely long. For the total energy of all wave-lengths we have

$$\int_{-\infty}^{+\infty} \frac{\sin^2 \pi r n}{n^2} dn = \pi^2 r. \quad (2)$$

That the total energy should be proportional to r is what we would expect. The maximum coefficient in (1) occurs, of course, when $n = 0$, and is proportional to r^2 ; once proportional to r on account of the greater total energy as given in (2), and again on account of the greater *condensation* of the spectrum as r increases. Expression (1) may be taken to represent the spectrum of the radiation from a single molecule which describes in a given direction and with a given velocity a free path proportional to r . If there be N independent molecules answering to this description, N may be introduced as a factor into (1). From this expression Mr. Godfrey proceeds to investigate the spectrum corresponding to the aggregate radiation of the gas, integrating first for the different lengths (r) of parallel free paths described with constant velocity, and afterwards for the various component velocities across and in the line of sight, the latter giving rise to the Doppler effect. It is with the first of these integrations that I am more particularly concerned.

In order to effect it, we need to know the probabilities of the various lengths of free path described with given velocity. "Now, Tait has shown

that, of all atoms moving with velocity v , a fraction $e^{-f\rho}$ penetrates unchecked to distance ρ where f is [a function of v and of the permanent data of the gas]. From this we see that, of molecules moving with velocity v , a fraction $fe^{-f\rho}d\rho$ have free paths between ρ and $\rho + d\rho$. Now, such a molecule will emit an undisturbed train of waves of length between r and $r + dr$, where $r = \rho \cdot V/v$, and V is the velocity of light. Hence, of all molecules moving with velocity v , a fraction $(fv/V)e^{-v^2r/V}$ will give free paths between r and $r + dr$. Returning to the expression (1) for the energy of a single train of length r , we see that with the aggregates of molecules now under consideration (definite thwart and line-of-sight velocities) we have for n a proportion of energy

$$\frac{fv}{n^2V} \int_0^\infty e^{-v^2r/V} \sin^2 n\pi r \cdot dr,$$

or, on effecting the integration,

$$\frac{2\pi^2}{4\pi^2n^2 + v^2f^2/V^2}. \quad (3)^*$$

The next steps are integrations over the various velocities, but it is not necessary to follow them here in detail, inasmuch as the objection which I have to take arises already. It appears to me that what we are concerned with is not the momentary distribution of free paths among the molecules which are describing them, but rather the statistics of the various free paths (described with velocity v) which occur in a relatively long *time*. During this time various free paths occur with frequencies dependent on the lengths. Fix the attention on two of these, one long and one short. They present themselves in certain relative numbers, or say in a certain proportion, and it is with this proportion that we have to do. The other procedure takes, as it were, an instantaneous view of the system and, surveying the molecules, inquires what proportions of them are pursuing free paths of the two lengths under contemplation. It is not difficult to recognise that this is a different question. Of the paths which are described in a given period of time, an instantaneous survey is more likely to hit upon a long one than upon a short one. Thus Mr. Godfrey's integration favours unduly the long paths.

The above consideration indicates that we ought to divide by r previously to integration, that is, evaluate

$$\frac{fv}{n^2V} \int_0^\infty r^{-1} e^{-v^2r/V} \sin^2 n\pi r \cdot dr. \quad (4)$$

If we write

$$\int_0^\infty r^{-1} e^{-ar} \sin^2 ar \cdot dr = y,$$

* Mr. Godfrey's expression (iii) differs somewhat from (3). A $4\pi^2$ appears to have been temporarily dropped, but this is not material for my present purpose.

we find

$$\frac{dy}{da} = \frac{2a}{4a^2 + c^2},$$

and

$$y = \frac{1}{4} \log \frac{4a^2 + c^2}{c^2}.$$

Hence

$$(4) = \frac{fv}{4n^2V} \log \left\{ 1 + \frac{4n^2\pi^2V^2}{v^2f^2} \right\}, \quad (5)$$

in place of (3).

It must be remarked, however, that an over-valuation of long paths relatively to shorter ones which all correspond to the same velocity would not of itself explain the 10-per-cent. discrepancy; for, when the gas is infinitely rare, all the paths must be considered to be infinitely long, and then the proportion of relatively longer and shorter paths becomes a matter of indifference. In fact (3) should give the correct result in the limit ($f = 0$), even though it be of erroneous form as respects n , provided a suitable function of f and v be introduced as a factor. If we integrate (3) as it stands with respect to n between the limits $-\infty$ and $+\infty$, we obtain

$$\frac{2\pi^2V}{vf}. \quad (6)$$

But this should certainly be independent of f . I think that if we introduce the factor vf into (3), Mr. Godfrey's analysis would then lead to the same result as is obtained by neglecting the influence of collisions *ab initio*.

It may be convenient to recite the constitution and visibility of a spectrum line according to the simple theory, where the Doppler effect is alone regarded. If ξ be the velocity of a molecule in the line of sight, the number of molecules whose velocities in this direction lie between ξ and $\xi + d\xi$ is, by Maxwell's theory,

$$e^{-\frac{1}{2}\xi^2} d\xi. \quad (7)$$

According to Doppler's principle the reciprocal wave-length of the light received from these molecules is changed from Λ^{-1} , corresponding to $\xi = 0$, to $\Lambda^{-1} (1 + \xi/V)$, V being the velocity of light. If x denote the variation of reciprocal wave-length, $x = \Lambda^{-1}\xi/V$, and the distribution of light in the dilated spectrum line may be taken to be

$$e^{-\Lambda^2 V^2 x^2} dx. \quad (8)$$

When this light forms interference-bands with relative retardation D , the "visibility" accorded to Michelson's reckoning is expressed by

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$$\int_{-\infty}^{+\infty} e^{-\lambda V^2 \Lambda^2 x^2} \cos(2\pi D x) dx + \int_{-\infty}^{+\infty} e^{-\lambda V^2 \Lambda^2 x^2} dx,$$

that is

$$e^{-\frac{\pi^2 D^2}{\lambda V^2 \Lambda^2}}. \quad (9)$$

If v be the velocity of mean square, on which the pressure of the gas depends,

$$v^2 = \frac{3}{2h}. \quad (10)$$

In terms of v the exponent in (8) is

$$-\frac{3V^2 \Lambda^2 x^2}{2v^2}, \quad (11)$$

and that in (9) is

$$-\frac{2\pi^2 v^2 D^2}{3V^2 \Lambda^2}. \quad (12)$$

*An Experiment with the Balance to Find if Change of Temperature
has any Effect upon Weight.*

By J. H. POYNTING, Sc.D., F.R.S., and PERCY PHILLIPS, M.Sc.

(Received July 12, 1905.)

In all the experiments hitherto made to determine the gravitative attraction between two masses, the temperature has not varied more than a few degrees, and there are no results which would enable us to detect with certainty any dependence of attraction upon temperature even if such dependence exists. It is true, as Professor Hicks has pointed out,* that Baily's results for the Mean Density of the Earth, if arranged in the order of the temperature of the apparatus when they were obtained, show a fall in value as the temperature rises. But this is almost certainly some secondary effect, due to errors in the measurements of the apparatus, or to the seasons at which different attracted masses were used.†

The ideal experiment to find if temperature has an effect on gravitation would consist in one determination of the gravitative attraction between two masses at, say 15° C., and another determination at, say, the temperature of boiling liquid air. But the difficulties of exact determination at ordinary temperatures are not yet overcome, and at any very high or very low temperatures, they would be so much increased that the research seems at present hopeless.

The question can, however, be attacked in a somewhat less direct method by examining whether the weight of a body—the gravitative attraction of the earth upon it—varies when the temperature of the body varies. The various parts of one of the attracting masses—the Earth—remain, each part, at the same temperature throughout, and this is, no doubt, a weakness of the method. For it is perhaps conceivable that in the expression for the attraction a temperature factor might exist of some such form as $1 + \kappa(Mt + mt')/(M + m)$, where M and m are the two masses, and t and t' are their temperatures. If m/M is negligible, this reduces to $1 + \kappa t$, and is independent of the temperature t' of the smaller mass. But it seems more likely that each mass would have a separate temperature factor. If such a factor exists, and if its variation is appreciable, then we ought to be able to detect a change of weight with change of temperature.

Observations on pendulums suffice to show that at the most any such effect

* 'Proc. Camb. Phil. Soc.,' vol. 5, p. 156.

† Poynting, "Mean Density of the Earth," p. 56.

must be small. The nearly constant period of vibration with the nearly constant length of a compensated or an "invar" pendulum shows constancy of weight of the bob to a considerable degree of exactness. Again, the agreement of weight methods and volume methods of measuring the expansion of liquids with rise of temperature show, though less conclusively, that there is no great variation.

It appeared to us that it would be possible to go much further in testing constancy of weight by a direct weighing experiment, in which the weight on one side of a balance should be subjected to great changes of temperature while the counterpoise should remain at a uniform temperature. We give an account in this paper of a series of experiments carried out on the following principle. A brass cylinder weighing 266 grammes was hung by a wire from one arm of a balance so as to be near the bottom of a tube depending from the floor of the balance case, the tube being closed at the bottom and opening at the top into the case, the wire passing down through the opening. The brass cylinder was counterpoised by an equal cylinder hung by a short wire from the other arm inside the case. To this short wire was attached a finely divided scale on which the swings of the balance could be read by a microscope looking through a window in the case. The balance was released and left free to swing. Then the case was exhausted till the pressure was not more than a small fraction of a millimetre of mercury. Steam was passed round the lower part of the tube where the weight hung, and after a time the weight was allowed to cool again. In other experiments the lower part of the tube was cooled by liquid air and again brought up to the temperature of the room.

While the changes of temperature were in progress there were considerable apparent variations in weight. But ultimately, when the temperature became steady, the weight, too, became steady. At 100°C . it was slightly less than at the temperature of the room. This difference was partly due to a rise in the temperature of the case, such a rise being always accompanied by an apparent diminution of the weight in the tube, whether steam was applied or the balance was merely left to follow the temperature of the room. Probably this effect was due to some change in the balance beam. But the difference was partly due to convection currents, or at any rate to the residual air in the case, for it varied with the disposition of diaphragms in the tube. There were no doubt convection currents, as there was always a tendency for the case to rise in temperature when steam was applied, and this could hardly be accounted for by conduction or radiation, under the conditions of the apparatus. As effects due to residual air should depend upon surface and not upon volume, similar experiments were made with hollow weights, each

about 58 grammes, and of the same size and form as the solid weights. There was again an apparent diminution in weight when steam was applied. Any true diminution due to change of temperature should be shown by a difference in the diminution with the solid and with the hollow weights, the surface effects being eliminated, and this diminution should be that of $266 - 58 = 208$ grammes.

The net result of all the experiments was that there was not a greater change in 208 grammes between 15° C. and 100° C., than 0.003 milligramme. But an inspection of the detailed account given later shows that this result is probably accidentally small—within the limits of experimental error. It would imply that there is not a change greater than 1 in 6×10^9 per 1° C. But the experiments hardly justify us in saying more than that there is not a change greater than 1 in 10^9 per 1° .

When liquid air was used, air currents were absent, and the temperature variations of the case were much less. The net result of these experiments was that there is not a change of weight in 208 grammes between 16° C. and -186° C. greater than 0.002 milligramme. This would imply that there is not a change greater than 1 in 1.3×10^{10} per 1° change of temperature. We may probably assert that the change is not greater than 1 in 10^{10} per 1° C.

We now proceed to a detailed account of the apparatus and of the mode of using it.

The Balance.

The balance has a 6-inch beam and was specially constructed for the experiment by Mr. Oertling. The general arrangement will be seen from fig. 1. The base plate is of gunmetal, as are also two sides and the top of the case. The front and back of the case are of thick plate glass fixed to the metal by marine glue. In the experiments the base plate was supported on levelling screws on a slate slab, and between it and the slab was a gas pipe with pinhole burners so that it could be warmed. When the case was to be fixed in position the jets were lighted and sealing wax was smeared on to the area of contact of plate and case. When the wax was quite liquid the case was put down on the plate and the gas was turned off. When the metal was cool the joint was perfectly air-tight.

The tube T in which the weight W hung was of brass, 4.1 cm. internal diameter and 62.5 cm. long. It consisted of three parts. The topmost was brazed to the base plate and the two lower parts were attached to it and to each other by flanged joints *ff*. Between the flanges was placed a circular lead washer of diamond shaped section. When the flanges were pressed together by bolts the joint was quite air-tight. Round the middle section of

the tube was a water jacket *wj* through which water flowed while an experiment was in progress, and round the lowest section was a steam jacket *sj* through which either water or steam could be passed. This jacket could be removed and could be replaced by a vacuum vessel 30 cm. long containing liquid air.

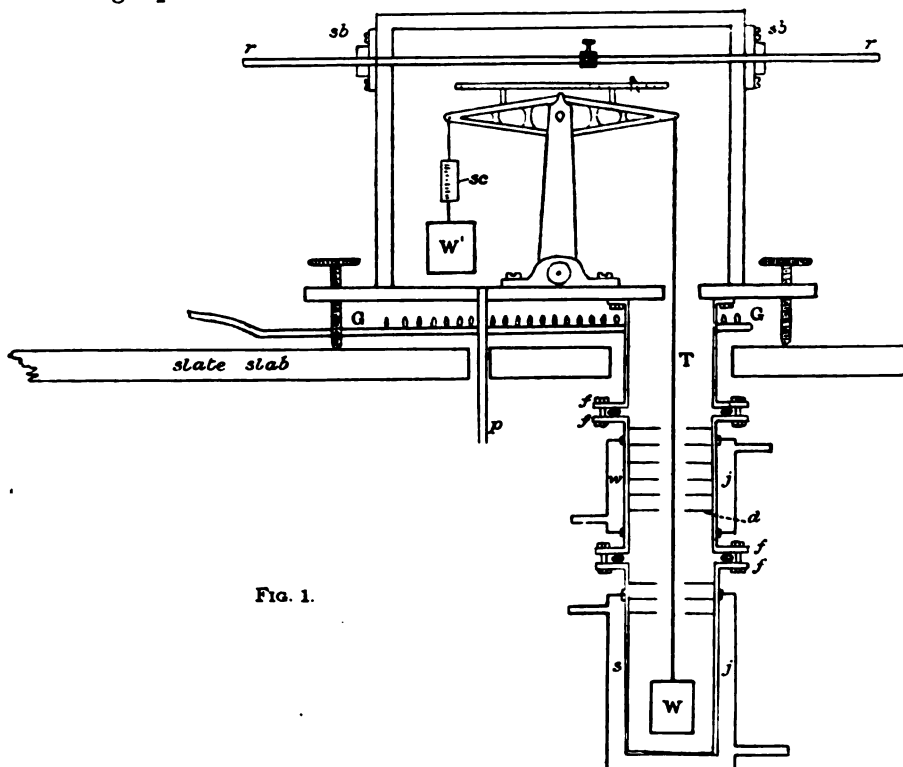
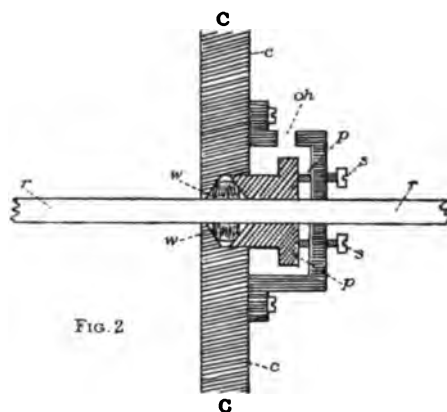


FIG. 1.

- W*, weight of which the temperature is to be raised, *W'* counterpoise.
T, tube in which it hangs, with a number of diaphragms with $\frac{1}{4}$ -inch holes.
sj, steam jacket, replaced by liquid air jacket.
ff, flanged joint with lead washer.
wj, water jacket.
p, pipe to the exhausting pump.
sc, scale read by a microscope not shown.
rr, rider rod passing through stuffing boxes, *sb*, enlarged in fig. 2.
gg, gas burners to heat the base plate before sealing up.

The weights *W W'* were turned from the same gunmetal bar. The length of each was 4.45 cm. the diameter 3 cm. and the solid weights were each 266.17 grammes, while the hollow ones were 57.86 grammes. They were hung directly from the end plates of the balance by platinum wires, and any residual inequality was compensated by moving a centigramme rider along the

beam by the rider rod *rr*. This rod passed through stuffing boxes *sb*, designed for us by Mr. G. O. Harrison, the mechanical assistant in the laboratory, to whom we are much indebted for this and many other valuable suggestions, and for the careful construction of all the apparatus except the balance. These stuffing boxes were perfectly air-tight when screwed up and the rod could still be rotated without any leakage. But to draw it in or out it was necessary to loosen the screws slightly, and in one case when this was done some leakage occurred. As the construction appears to give an efficient mode of moving apparatus inside a vacuum from without, we give in fig. 2 a section of a stuffing box.



- rr*, rider rod.
CC, side of case.
ww, two or three circular washers punched out of soft leather and soaked in oil.
p, plunger driven in by screws, *ss*.
oh, oil hole through which valvoline, a thick lubricating oil, was inserted.

The position of the balance beam was read by a microscope viewing a glass scale *sc*, fig. 1, interposed in the suspension of *W'*. The scale was divided to 0.1 mm. and numbered in millimetres. The objective of the microscope was placed inside the case and the eye-piece with cross hairs was fixed outside it. The axis of the microscope was horizontal and a lamp at the back illuminated the scale. The case was surrounded by felt and a tin cover was placed over the whole, small windows through the felt then allowing the scale to be seen. A thermometer placed between the felt and the case was taken to give the temperature of the case.

A brass pipe *p* from the floor of the case led to the pumping apparatus. This pipe was connected to a branched glass tube, one branch going to a Fleuss pump and the other to a 4-fall Sprengel, made continuous in its action by a steel pump which was worked by a motor, and which raised the mercury

again from the cistern at the base to the reservoir at the top. When the case was to be exhausted the Fleuss pump was first used and then sealed off and the exhaustion was carried on by the Sprengel. The degree of exhaustion was estimated by sending a discharge through a vacuum bulb 10 cm. diameter connected with the tube to the pump, and usually the pumping was continued till the negative dark space was of the order of 4 cm. As a rule the vacuum held without serious change for days or even for weeks.

Mode of Experiment.

A large number of preliminary experiments were made with a pair of brass weights each about 187 grammes. These were only useful in bringing to the front the difficulties in obtaining good results and in suggesting means for overcoming them. We shall only record the final results with the 266 grammes and 58 grammes weights.

The weights and the lower section of the tube were first cleaned by boiling in caustic potash solution and washing in distilled water. They were then suspended, being handled with gloves only, and the lowest section of the tube was screwed on.

Steam Heating.

The jacket *sj* (fig. 1) was fixed on the lower section of the tube and the balance was set free to vibrate, being left free during a whole series of experiments. The case was then sealed on and the value of a scale division was determined by the rider. Any change in the value during a series could be determined from the change in period of the swing. The time of swing in different series ranged from 24 to 42 seconds. After the stuffing boxes were tightened the case was exhausted till the pressure was estimated to be not more than $\frac{1}{16}$ mm. of mercury. The weight of air displaced by a weight was then of the order 0.001 milligramme and the change in this with change of temperature was quite negligible.

Cold water was passed through the water jacket *wj*, and sometimes, while steam was being got up in a boiler at some distance well screened from the balance, through *sj* also. The centre of swing and the temperature of the case were observed, and before any heating occurred the balance was usually quite steady. Steam was then blown through *sj*, water still flowing through *wj*. After considerable changes, which will be described later, the centre of swing in the course of five or six hours settled down to a steady march which appeared to correspond to change in temperature of the case. Sometimes steam was turned off after eight or nine hours, but in some cases it was kept on for 24 and 48 hours and even longer. Then it was turned off and the

jacket was allowed to cool. The centre of swing was observed when steady, several hours later or next day.

The results in the first few heatings and coolings after an exhaustion of the case were rejected, as there was evidence that the earlier heatings drove gas from the weight. Only after successive heatings gave fairly consistent values were these taken into account.

One effect of the steam heating was always to raise the temperature of the case, probably through convection of the residual air. A rise of temperature in the case was always accompanied by a lowering of the scale reading, corresponding to a diminution in weight. The effect was somewhat irregular, but an average value of the lowering per 1° rise was determined by observing the centre of swing of the balance at intervals through several days, when the balance was left to follow the varying temperature of the room and no steam was flowing. The value thus obtained was used to correct all the readings to 15° C.

As an example of the method pursued, we give in Table I the series of readings used to obtain the temperature correction for the hollow weights.

Table I.—Change of Centre of Swing with Change of Temperature of Case.

Date.	Time.	Centre of swing in millimetres of scale.	Temperature of case.
6.12.04	1.0 P.M.	14.34	14.75
"	3.0 "	14.355	14.55
"	5.40 "	14.35	14.65
7.12.04	12.35 "	14.51	12.70
"	5.5 "	14.465	13.60
8.12.04	11.5 A.M.	14.43	14.70
"	12.55 P.M.	14.20	14.95
9.12.04	9.51 A.M.	14.555	12.80
"	2.27 P.M.	14.525	13.3
10.12.04	9.37 A.M.	14.46	15.0

The temperature correction deduced from these numbers by the method of least squares is a decrease of 0.13 division per 1° C. rise, and as the sensibility was 1 division for 0.248 milligramme, there was an apparent decrease of weight of 0.032 milligramme per 1° rise.

Two similar series with the solid weights gave a decrease of 0.044 division per 1° C. rise, and as the sensibility was now 1 division per 0.803 milligramme, there was an apparent decrease of weight of 0.035 milligramme per 1° rise.

Another series with the solid weights when steam was passing all the time for several days, gave a decrease of 0.052 division per 1° rise, but as the

values were more irregular, the series giving 0.044 division were used. This series with steam sufficed to show that very nearly the same temperature correction applied when the weight was hot as when it was cold.

The irregularity of the observations is only to be expected when it is remembered that the balance was subjected to some considerable vibration at times through machinery running in the same building, and that the observations extended over several days. Indeed it is remarkable that there was not more irregularity, and the fair consistency of the observation illustrates once more the marvellous accuracy of a well-made balance.

The following Table II will serve as an example of a complete experiment in which one of the hollow weights was cold initially, was then surrounded with steam for 24 hours, and was then allowed to get cold again. The observations recorded are at about hourly intervals, but intermediate ones, not used, were frequently taken to be sure that there were no sudden changes.

Table II.—Experiment with Hollow Weight raised to 100° C. and then cooled,
1 mm. = 0.248 milligramme.
Correction for temperature of case — 0.13 division per 1°.

Date.	Time.	Condition of weight.	Centre of swing, 1 = 1 mm.	Temperature of case.	Centre of swing corrected to 15° C.	Remarks.
17.11.04	9.25 A.M.	Cold	14.905	14° 75	14.872	Steam put on just after 9.25 and kept on till 10 A.M. next day.
"	4.0 P.M.	Hot	14.40	15.0	14.400	
"	5.20 "	"	14.39	15.0	14.390	
"	6.12 "	"	14.375	15.0	14.375	
"	7.8 "	"	14.365	15.05	14.372	
"	7.56 "	"	14.36	15.1	14.373	
18.11.04	9.5 A.M.	"	14.30	15.05	14.307	Steam turned off just after 9.55.
"	9.55 "	"	14.295	15.1	14.308	
"	5.36 P.M.	Cold	14.55	16.00	14.680	
"	6.39 "	"	14.56	15.95	14.684	
"	7.56 "	"	14.58	15.75	14.678	
19.11.04	9.40 A.M.	"	14.67	14.80	14.579	
"	11.38 "	"	14.665	14.20	14.561	

Initial reading, cold at 15° 14.872 divisions.
 Final mean reading, cold at 15° ... 14.636 "
 Mean reading, cold 14.754 "
 " hot 14.360 "
 Cold—hot 0.394 division.

The following Table III gives the results of the various experiments with the hollow weight, treated as in Table II, the readings of the centre of swing being at about hourly intervals when on the same day.

Table III.—Experiments with Hollow Weight raised to 100° C. and then cooled,
1 mm. = 0.248 milligramme.

Correction for temperature of case — 0.044 division per 1°.

Date.	Condition of weight.	Centre of swing corrected to 15°.	Number of readings from which centre of swing is found.	Greatest deviation from the mean.	Excess of cold above hot.	Remarks.
16.11.04	Hot	14.749	4	0.020	0.123	Temperatures 14°·75 to 16°·8. The initial cold reading was rendered useless by a subsequent shift of scale reading, probably due to slight displacement of the eye-piece.
17.11.04	Cold	14.872	1	—		
17.11.04	Cold	14.872	1	—	0.394	Temperatures 14°·2 to 16°. The set given in full in Table II. The last of the preceding used as the first of this.
17—18.11.04	Hot	14.360	7	0.058		
18—19.11.04	Cold	14.686	5	0.075		
21.11.04	Cold	14.218	1	—	0.165	Temperatures 10°·45 to 14°·8.
22—23.11.04	Hot	14.091	6	0.095		
23.11.04	Cold	14.294	3	0.040		
25.11.04	Cold	14.421	1	—	0.187	Temperatures 10°·95 to 14°·5.
"	Hot	14.029	2	0.001		
26.11.04	Cold	14.010	2	0.016		
1.12.04	Cold	14.500	1	—	0.334	Temperatures 16° to 16°·9.
"	Hot	14.100	3	0.007		
2.12.04	Cold	14.367	1	—		
2.12.04	Cold	14.367	1	—	0.166	Temperatures 16°·9 to 17°·45.
2—3.12.04	Hot	14.218	3	0.048		
3.12.04	Cold	14.400	1	—		
12.12.04	Cold	14.379	1	—	0.279	Temperatures 13°·65 to 15°·75.
"	Hot	14.106	3	0.018		
13.12.04	Cold	14.390	1	—		

Mean value cold—hot = 0.235 division = 0.058 milligramme.

The following Table IV gives the results with the solid weight. They are not so consistent as those with the hollow weight, probably because they were spread over a longer time on the average. This was done to secure that the weight should be more nearly at the temperature of its surroundings. A rough estimate shows that if heat be gained by radiation alone and the brass is taken as a full radiator, three hours will be required to bring it within 1° of the temperature of the steam. The last two experiments were incomplete in that no final cold weighing was taken, but the results obtained were regarded as probably sufficient.

Table IV.—Experiments with Solid Weight raised to 100° and then cooled,
1 mm. = 0.803 division.

Correction for temperature of case —0.044 division per 1°.

Date.	Condition of weight.	Centre of swing corrected to 15°.	Number of readings from which centre of swing is found.	Greatest deviation from the mean.	Excess of cold over hot.	Remarks.
26.12.04	Cold	16.295	1	—		Temperatures 9°.9 to 11°0.
27—28.12.04	Hot	16.032	2	0.017	0.189	
29.12.04	Cold	16.046	1	—		
30.12.04	Cold	16.016	1	—		Temperatures 9°1 to 12°05.
30—31.12.04	Hot	15.914	4	0.021	0.112	
2.1.05	Cold	16.035	1	—		
2.1.05	Cold	16.035	1	—		Temperatures 9°1 to 12°1.
3.1.05	Hot	16.022	2	0.018	0.019	
4.1.05	Cold	16.047	1	—		
5.1.05	Cold	15.987	1	—		Temperatures 11°95 to 12°65. Experiment interrupted by stoppage of steam tubes.
„	Hot	15.919	3	0.002	0.068	
9.1.05	Cold	16.048	1	—		Temperatures 13°7 to 15°65. Heating continued several days after this to obtain temperature correction. No final cold reading taken.
10.1.05	Hot	16.039	4	0.020	0.009	

Mean value cold—hot = 0.069 division = 0.055 milligramme.

From Tables III and IV we have—

Solid weight, 266 grammes: cold—hot = 0.055 milligramme.

Hollow weight, 58 grammes: cold—hot ... = 0.058 „

For the difference, 208 grammes: hot—cold = 0.003 „

Taking the rise in temperature as 85°, this gives a change of the order of 1 in 6×10^9 per 1° rise. But evidently the smallness of the result is accidental, and probably all we can assert from the work is that any change of weight with change of temperature between 15° C. and 100° C. is not greater than 1 in 10^9 .

Cooling with Liquid Air.

Experiments were made in which heating by steam was replaced by cooling with liquid air. This was supplied to us by Sir William Ramsay, and we desire to express our hearty thanks to him for his ready kindness in helping us to increase the temperature range so considerably. In these experiments the steam jacket was removed and replaced by a vacuum vessel 30 cm. deep and 6 cm. inside diameter, kept full of liquid air. After the

steady state was reached the liquid air was removed, the jacket was replaced and cold water was again passed round the tube.

Owing to the evaporation of the air the experiments had to be carried out more rapidly than those with steam, but through the absence of convection currents, a steady state was more rapidly reached, and the variation in the temperature of the case was very small.

The temperature correction was not observed, but as in the subsequent observations with both solid and hollow weights, it was found to be about 0.03 milligramme per 1° , this value was assumed to hold here. In any case its effect is very small, as the temperature varied so little.

The centre of swing was observed nearly continuously from the time when the liquid air was applied and again after it was removed. After a time in each case it became steady and only these steady values are recorded in the following Tables.

Table V.—Experiment with Solid Weight cooled by Liquid Air,
1 mm. = 0.315 milligramme.

Correction for temperature of case -0.1 division per 1° .

Date.	Time.	Condition of weight.	Centre of swing.	Temperature of case.	Centre of swing corrected to 16°6.	Remarks.
28.7.04 ...	3.25 P.M.	Normal	11.085	16° 6	11.085	Liquid air applied just after 3.25.
" ...	5.50 "	Cold	11.07	16° 65	11.075	
" ...	6.0 "	"	11.07	16° 65		11.075
" ...	6.10 "	"	11.07	16° 65		
" ...	8.45 "	Normal	11.095	16° 4		
" ...	9.15 "	"	11.095	16° 4		

Normal—cold = 0.005 division = 0.0016 milligramme.

Table VI.—Experiment with Hollow Weight cooled by Liquid Air,
1 mm. = 0.343 milligramme.

Correction for temperature of case -0.1 division per 1° .

Date.	Time.	Condition of weight.	Centre of swing.	Temperature of case.	Centre of swing corrected to $16^{\circ}6$.	Remarks.
9.9.04 ...	9.40 A.M.	Normal	14.485	$16^{\circ}3$	14.455	Liquid air applied at 9.43.
" ...	11.40 "	Cold	14.480	$16^{\circ}4$	14.460	
" ...	11.50 "	"	14.480	$16^{\circ}4$	14.460	Removed at 11.52.
" ...	5.25 P.M.	Normal	14.480	$16^{\circ}4$		Steady. The balance next morning read 14.48 at $16^{\circ}3$.

Normal—cold = -0.002 division = -0.0007 milligramme

From Tables V and VI we have—

Solid weight, 266 grammes: normal—cold ... = 0·0016 milligramme.

Hollow weight, 58 grammes: normal—cold ... = -0·0007 „

For the difference, 208 grammes: normal—cold = 0·002 „

Taking the fall in temperature as 200° , this gives a change of the order of 1 in 2×10^{10} per 1° fall.

These liquid air experiments were not repeated. But the conditions are probably much less disturbed than with the steam experiments, and we may safely say that if there is any change of weight with change of temperature between $16^{\circ}6$ C. and -186° C., it is not so great as 1 in 10^{10} per 1° C.

Note on the Change of Apparent Weight on First Heating or Cooling.

We have mentioned that while the changes in the temperature of the weight were in progress there were considerable apparent variations in weight. These, in a few cases, amounted to as much as 0·6 milligramme. They were almost certainly due to radiometric forces or to other gas action, for they were very dependent on the disposition of the diaphragms in the tube T (fig. 1), and also on the way in which the steam was blown through the jacket.

In the preliminary experiments with solid weights the lowest diaphragm was 5 to 6 inches above the weight, and the steam was blown into the top of the jacket. Under these circumstances the following variations occurred when the steam was turned on:—

At first the weight apparently increased, until in 15 to 20 minutes it reached a maximum, which was in some cases as much as 0·6 milligramme above the real weight. After reaching this maximum the weight apparently decreased, till in four hours it had reached a nearly steady value, which was a little less than the value at the temperature of the laboratory.

If, now, the jacket was filled with cold water, the apparent weight first increased for about one minute and then decreased for about two hours to a minimum, which was a little lower than the final weight at 100° . After this the weight very slowly increased, till in five to six hours it had recovered the value which it had before the experiment.

These changes did not vary very much with the pressure, but at lower pressures they took place more rapidly than at higher ones.

On cooling the weight with liquid air changes occurred exactly similar to those which occurred when the weight was cooled from 100° to the temperature of the laboratory; and when the weight was warmed up from the temperature of liquid air to the temperature of the laboratory, the

changes were similar to those when the weight was warmed from the temperature of the laboratory to 100° C.

So long as the arrangement of the diaphragms and the weight remained the same, and so long as the steam was blown through in the same way, these changes were exactly similar, but as soon as any alteration was made in these arrangements the character of the changes altered.

In one series of experiments a sealed glass bulb containing mercury was used in place of the brass weight. In this case, immediately after the steam was turned on there was a rapid decrease in weight, and a minimum was reached in less than one minute. After this the changes were very similar to those occurring with the brass weight. On cooling, however, the changes were almost exactly the reverse of the changes on heating, and were not at all like the changes with the brass weight.

In the final experiments, those recorded, the lowest diaphragm was within $\frac{1}{8}$ -inch of the top of the brass weight. With this arrangement and with the steam blown into the top of the jacket, the following changes occurred:—

The apparent weight first increased rapidly, reaching a maximum in about one minute, then it rapidly decreased, reaching a minimum in about four minutes, and again increased to another and lower maximum in 8 to 10 minutes. After this it slowly decreased to a nearly steady value a little lower than the original value.

On passing cold water through the jacket the apparent weight rapidly increased for about one minute, and then slowly decreased to its original value.

Still another variation was arranged by blowing the steam in at the bottom of the jacket instead of at the top, all the other things remaining as in the last experiment.

In this case, on turning on the steam, the apparent weight first decreased to a minimum in about one minute, then increased to a maximum in about six minutes, and finally decreased slowly to a nearly steady value a little below the original value.

The cooling and the consequent changes were exactly similar to those in the last experiment.

It is somewhat difficult to follow out exactly the changes which would be caused by radiometer action and by convection currents in these different arrangements of the apparatus, but the fact that these changes depend entirely on the arrangement, is sufficient evidence that they are caused by gas action, and, as we have before said, we have some reason to believe that even the small final difference is due to air currents.

A New Formation of Diamond.

By Sir WILLIAM CROOKES, Hon. D.Sc. (Oxford and Dubl.), F.R.S.

(Received July 20, 1905.)

Boiling-Point and Melting-Point of Carbon.

On the average the critical point of a substance is 1·5 times its absolute boiling-point. Therefore the critical point of carbon should be about 5800° Ab. But the absolute critical temperature divided by the critical pressure is for all the elements so far examined never less than 2·5; this being about the value Sir James Dewar finds for hydrogen. So that, accepting this, we get the maximum critical pressure as follows, viz., 2320 atmospheres:—

$$\frac{5800^{\circ} \text{ Ab.}}{\text{CrP}} = 2\cdot5, \text{ or } \text{CrP} = \frac{5800^{\circ} \text{ Ab.}}{2\cdot5}, \text{ or } 2320 \text{ atmospheres.}$$

Carbon and arsenic are the only two elements that have a melting-point above the boiling-point; and among compounds carbonic acid and fluoride of silicium are the only other bodies with similar properties. Now the melting-point of arsenic is about 1·2 times its absolute boiling-point. With carbonic acid and fluoride of silicium the melting-points are about 1·1 times their boiling-points. Applying these ratios to carbon we find that its melting-point would be about 4400°.

Therefore, assuming the following data,

Boiling-point	3870° Ab.
Melting-point	4400°
Critical temperature	5800°
Critical pressure	2320 Ats.

the Rankine or Van der Waals formula calculated from the boiling-point and critical data would be as follows:—

$$\log P = 10\cdot11 - 39120/T,$$

and this gives for a temperature of 4400° Ab. a pressure of 16·6 Ats. as the melting-point pressure.

The results of the formula are given in the form of a table:—

Temperature	Pressure.	
Ab.	Ats.	
3870°	1·00	Boiling-point.
4000°	2·14	
4200°	6·25	
4400°	16·6	Melting-point.
4600°	40·4	
4800°	91·2	
5000°	193	
5200°	386	
5400°	735	
5600°	1330	
5800°	2320	Critical point (15 tons per square inch).

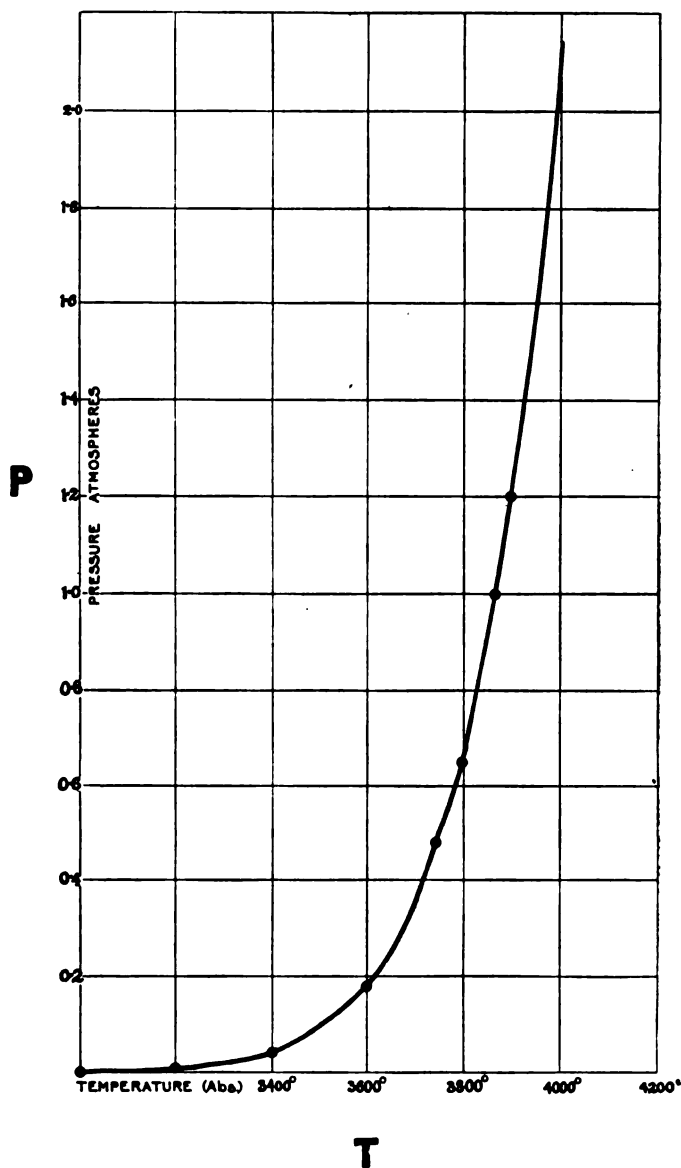
If then we may reason from these rough estimates, above a temperature of 5800° Ab. no amount of pressure will cause carbon vapour to assume liquid form, whilst at 4400° Ab. a pressure of above 17 atmospheres would suffice to liquefy some of it. Between these extremes the curve of vapour pressure is assumed to be logarithmic, as represented in the accompanying diagram. The constant 39120 which occurs in the logarithmic formula enables us to calculate the latent heat of evaporation. If we assume the vapour density to be normal, or the molecule in vapour as C_2 , then the heat of volatilisation of 12 grammes of carbon would be 90,000 calories; or, if the vapour is a condensed molecule like C_6 , then the 12 grammes would need 30,000 calories. In the latter case the evaporation of 1 gramme of carbon would require 2500 calories, whereas a substance like zinc needs only about 400 calories.

A New Formation of Diamond.

I have long speculated as to the possibility of obtaining artificially such pressures and temperatures as would fulfil the above conditions. In their researches on the gases from fired gunpowder and cordite, Sir Frederick Abel and Sir Andrew Noble obtained in closed steel cylinders pressures as great as 95 tons to the square inch, and temperatures as high as 4000° C. According to a paper recently communicated to the Royal Society, Sir Andrew Noble, exploding cordite in closed vessels, has obtained a pressure of 8000 atmospheres, or 50 tons per square inch, with a temperature reaching in all probability 5400° Ab.

Here, then, we have conditions favourable for the liquefaction of carbon, and were the time of explosion sufficient to allow the reactions to take place, we should certainly expect to get the liquid carbon to solidify in the crystalline state.*

* Sir James Dewar, in a Friday Evening Discourse at the Royal Institution, 1880,



showed an experiment proving that the temperature of the interior of a carbon tube heated by an outside electric arc was higher than that of the oxy-hydrogen flame. He placed a few small crystals of diamond in the carbon tube, and, maintaining a current of hydrogen to prevent oxidation, raised the temperature of the tube in an electric furnace to that of the arc. In a few minutes the diamond was transformed into graphite. At first sight this would seem to show that diamond cannot be formed at temperatures above that of the arc. It is probable, however, for reasons given above, that at exceedingly high pressures the result would be different.

By the kindness of Sir Andrew Noble I have been enabled to work upon some of the residues obtained in closed vessels after explosions, and I have submitted them to the same treatment that Moissan's granulated iron had gone through.* After weeks of patient toil I removed the amorphous carbon, the graphite, the silica,† and other constituents of the ash of cordite, and obtained a residue among which, under the microscope, crystalline particles could be distinguished. Some of these particles, from their crystalline appearance and double refraction, were silicon carbide; others were probably diamonds. The whole residue was dried and fused at a good red heat in an excess of potassium bifluoride, to which was added during fusion 5 per cent. of nitre. (Previous experiments had shown me that this mixture readily attacked and dissolved silicon carbide; unfortunately it also attacks diamond to a slight degree.) The residue, after thorough washing and then heating in fuming sulphuric acid, was washed, dried, and the largest crystalline particles picked out and mounted. All the operations of washing and acid treatment were performed in a large platinum crucible by decantation (except the preliminary attack with nitric acid and potassium chlorate, when a hard glass vessel was used); the final result was washed into a shallow watch-glass and the selection made under the microscope.

From the treatment these crystals have undergone, chemists will agree with me that diamonds only could stand such an ordeal; on submitting them to skilled crystallographic authorities my opinion is confirmed. Speaking of one crystal (303), Professor Bonney calls it "a diamond showing octahedral planes with dark boundaries due to high refracting index." After careful examination, Professor Miers writes of the same crystal diamond:—"I think one may safely say that the position and angles of its faces, and of its cleavages, the absence of birefringence, and the high refractive index, are all compatible with the properties of the diamond crystallising in the form of an octahedron. Others of the remaining crystals, which show a similar high refractive index, appeared to me to present the same features."

It would have been more conclusive had I been able to get further evidence as to the density and hardness of the crystals; but I am still working at the subject, and hope to add these confirmatory tests. From what I have already said I think there is no doubt that in these closed-vessel explosions we have another method of producing the diamond artificially.

* 'Chemical News,' vol. 76, p. 14, July 9, 1897.

† The silica was in the form of spheres, perfectly shaped and transparent, mostly colourless, but among them several of a ruby colour. When 5 per cent. of silica was added to cordite, the residue of the closed-vessel explosion contained a much larger quantity of these spheres.

The Influence of Phase Changes on the Tenacity of Ductile Metals at the Ordinary Temperature and at the Boiling Point of Liquid Air.

By G. T. BEILBY and H. N. BEILBY, B.Sc.

(Communicated by Professor J. Larmor, Sec. R.S. Received July 20, 1905.)

[PLATE 5.]

The study of tenacity in metals has had so direct a bearing on the practical problems of metallurgy and engineering, that there is some risk that its scientific importance may be overlooked or lost sight of. It has occurred to us that the measurement of tenacity in solids may supply a direct means for the estimation of the cohesive force of the molecules at any given temperature, so that by the multiplication of observations at a variety of temperatures, it may become possible to estimate more and more closely the molecular cohesion at the absolute zero. The early observations of Dewar on the increase of tenacity at the boiling point of liquid air made it clear for the first time that the nature of the relation between tenacity and temperature continues unchanged even at the lowest attainable temperatures. The recent experiments of Hadfield supply further confirmation of this continuity. The metals used by these observers were almost always in the annealed or crystalline condition.

Tenacity in metals is measured, as is well known, by the tension required to tear asunder a rod, bar, or wire of the material. In ordinary mechanical tests of this kind it is assumed that the tensile stress is uniformly distributed over the whole surface at which rupture occurs; but this is only approximately true in the most favourable cases, while in many cases it is obviously untrue, as, for instance, when the surface of fracture is large relatively to the length of the specimen, or when the material is not homogeneous. It is not possible to experiment with a chain of single molecules, for even in the thinnest wire its smallest cross-section contains many millions of molecules. It follows, therefore, that only in a perfectly rigid body can all the pairs of molecules be pulled directly apart as they would be in a single chain. Any departure from perfect rigidity must involve that the molecules under strain will move over each other with a certain degree of freedom, as in the liquid state, and the rupture will become to some extent like that of a highly viscous liquid, *e.g.*, molten glass, in which the molecules evade any direct pull by slipping over each other.

The observations recorded in this paper are intended to prepare the way for a more direct attack on the problems of molecular cohesion, by the

establishment of clearer views as to the influence of changes of phase on the tenacity of ductile metals at various temperatures.

In a former paper on "The Hard and Soft States in Metal,"* the changes of state—from hard to soft and from soft to hard—were shown to be due to the changes of phase brought about in the one case by heat, and in the other by mechanical deformation or flow. In most, if not all, of the ductile metals the amorphous is the hard phase and the crystalline is the soft. This is contrary to the usually accepted ideas on the subject, for hardness and brittleness are generally supposed to be specially associated with the crystalline properties in metals. In reality the softest metals are those which pass most readily into the crystalline condition, and when in this condition they are at their softest stage. This particular softness is due to the readiness with which the crystals can be broken down again into the amorphous state; the crystalline is the phase of maximum instability under mechanical disturbance, while the amorphous is the thermally unstable phase. The ductile metals may be described as those which pass most readily from phase to phase: they are equally unstable mechanically and thermally.

Mechanical instability, and the phase-change on which it depends, is well illustrated in the stretching of wires under tension. Annealed wires, which are in the *C* phase, stretch when they are stressed beyond their yield point; hardened wires, which are partly in the *A* phase, do not stretch—they break without extension when their limit of tenacity is reached.

The homogeneous *C* phase as it occurs in a ductile metal which has been heated above the transition temperature, has no true breaking point; it yields and stretches when stressed beyond the elastic limit, and in so doing it passes partly into the *A* phase, and when rupture takes place it does so at the breaking stress of the mixed structure. The conditions under which this phase-change occurs may be very different, and the properties and structure of the mixture of phases which results vary with these altering conditions. A wire which has been hardened by simple stretching is different from one which has been hardened by hammering or by wire-drawing.

The tenacity of the mixed structure which results from plastic yielding which has taken place under favourable circumstances, approaches, but never quite reaches, the tenacity of the homogeneous *A* phase. To ascertain the true maximum tenacity of a pure metal it would be necessary to obtain it in this homogeneous condition. For the purpose we had in view it was necessary to obtain the metals as nearly as possible in this condition. It had previously been found† that only in the thinnest surface layers—probably from 50 to

* 'Phil. Mag.,' August, 1904.

† *Loc. cit.*

500 micro-millimetres in thickness—was it possible to obtain the metal in a perfectly structureless condition. Gold foil when beaten till it covers several times its original area becomes covered with a hard vitreous-looking surface film of extreme thinness, but the lightest of etching on this surface is sufficient to disclose a granular layer of mixed phases, and below this layer farther etching discloses the broken remains of crystalline grains and lamellæ.

By wire-drawing it is possible to destroy all traces of crystalline structure such as grains, lamellæ, or similarly oriented units, and to reduce the whole substance to a granular-looking condition. But in this condition the metal is not reduced to the homogeneous *A* phase, it is still an intimate mixture of the two phases. In a galvanic couple, consisting of the two phases of the same metal in a suitable solvent, the *A* phase dissolves before the *C* phase, which is, therefore, left as a skeleton of the former mixed structure. This then is what occurs when a hard-drawn wire is suitably etched, the vitreous surface layer dissolves first and discloses the granular structure below. By the continued action of the solvent the matrix in which the granules are embedded is removed, and these minute specks of *C* phase are left in the form of an extremely open structure.

After a wire has been stretched to four or five times its original length by drawing it through the conical holes of a wire plate, the substance of the metal is entirely reduced to the granular condition. Plate 5, fig. 1, *a* is a photograph of a gold wire which has been etched after drawing. The flow lines near the surface consist of rows of granules. *b*, on the same photograph, shows the effect of heating another piece of the same wire to about 400°. Removal of the surface by etching now discloses the fully developed crystalline grains with their differently oriented lamellæ. The thermal transformation from *A* to *C* has taken place and the wire is restored to the soft condition. Figs. 2 and 3 are photomicrographs at higher magnifications, which show the details of structure more fully. Fig. 2 is the granular structure by oblique light at a magnification of 250, and Fig. 3 is the crystalline structure by normal light, at a magnification of 700. The granular structure in 2 is so minute that it absorbs the normal illuminating rays to such an extent that it is not possible to obtain a satisfactory resolution by lenses of high numerical aperture. The granules seen on the photograph are not really the ultimate units, they are only aggregates of these. Fig. 3 shows very clearly the way in which each crystalline grain is built up of similarly oriented lamellæ, the orientation in each grain being different.

Heating merely to the transition temperature, while it changes the phase and softens the metal, does not quickly develop a well-marked crystalline

structure. This requires either a long time at the low temperature or the application of a considerably higher temperature for a short time.

The mechanical instability increases as the crystalline grains become larger and more fully developed, the yield point, therefore, varies with the condition of crystalline development.

As the primary object of these experiments was to bring each of the metals used into its highest state of tenacity, various methods of wire-drawing were tried to find that which would give the best results. It was realised that so long as the actual tension on the wire was accurately observed and its cross section accurately measured, those results which gave the highest tenacity were the best and most trustworthy. Under these conditions there was no danger of obtaining too high a result for any given metal, indeed, all the chances were the other way. But the purity of the metals was of great importance, for it is well known that minute traces of impurity may seriously affect the mechanical properties.

The metals used were, gold of a purity of 9997 parts per 10,000, silver of a purity of 10,000 parts per 10,000, and copper of a guaranteed conductivity of over 100 per cent. It was recognised that the purity of the copper was probably not quite of the same order as that of the gold and silver.

The tenacity tests were made by directly loading the stretched wire by a water load, so that the speed of loading and its smoothness could be easily regulated. In the experiments at the boiling point of liquid air, the wire with both grips was fully submerged in the liquid during the entire test. The extension was measured after the broken wires were removed from the grips. The diameter of the wires was measured by a micrometer screw gauge. For each wire the mean of a large number of measurements was taken, the measurements being usually taken in pairs on two diameters at right angles to each other. All the tenacity tests were made on wires of from 0.38 to 0.55 mm.

After annealing at a temperature rather above the transition point, the wire was drawn through a series of holes till it reached the desired diameter. The reduction of diameter and the increase of length were as a rule both directly measured. Wires were stretched in this way to as much as 15 times their original length when annealed. The minimum amount of stretching used was 1.4 times.

It was found possible to over-draw a wire so that its tenacity having passed a certain maximum began definitely to fall off. The highest tenacity in gold was developed by drawing it to $3\frac{1}{2}$ times its original length, but by drawing it to as much as 13 times the tenacity was only slightly reduced.

The maximum tenacities recorded at the ordinary temperature were—gold 15.6 tons per square inch, silver 25.7 tons and copper 28.4 tons.

At the boiling point of liquid air (-182°) the maxima were—Gold 22.4 tons per square inch, silver 34.4 tons, and copper 36 tons.

At the ordinary temperature none of the wires showed any general stretching. There was a slight extension of from 0.5 to 1 per cent., due entirely to a sharp reduction of diameter at the actual point of rupture. The diameter of the wires after breaking confirmed that there had been no general stretching.

At the boiling point of liquid air all the wires stretched from 11 to 12 per cent. This stretching affected the whole length of wire between the grips, and the diameter was correspondingly reduced. The tenacity was therefore always calculated on this reduced diameter.

The granular texture after this second stretching appeared slightly finer than that of the wires which broke without stretching, and it is believed that this revival of plasticity at the lower temperature is due to the further breaking down of the granules of *C* phase, which is rendered possible by the increased hardness and tenacity of the *A* phase. If the second stretching had taken place under the more favourable conditions of wire-drawing, it seems probable that there would have been a corresponding increase of the maximum tenacity at the low temperature.

We propose to test this question by actually drawing wires at the boiling point of liquid air. In this connection it is to be noted that experiments on wire-drawing at temperatures above 15° produced wires of lower tenacity; it appears probable, therefore, that for each metal there is a certain temperature at which wire-drawing will produce the maximum tenacity, and that, in the metals here referred to, that temperature is considerably below 15° , perhaps even below -182° .

The maximum tenacities recorded by Dewar and Hadfield are:—At the ordinary temperature, gold 15.1 tons per square inch, silver 19.5 tons, and copper 15 tons. At the boiling point of liquid air, gold 20.1 tons, silver 24.8 tons, and copper 20.1 tons. With the exception of the figures for gold, these tenacities are all considerably lower than those we have obtained. This was only to be expected, for the above tests on copper were made on the metal in the annealed condition. In the case of gold some further explanation appears to be called for. The tenacity of pure gold in the annealed state was found by Roberts-Austen to be 7 tons per square inch,* so that the specimen used in the observations by Dewar, if of equal purity, must have been in the hard-drawn, not in the annealed or crystalline condition.

A study of the form and appearance of the fractured ends of the wires used in our experiments reveals several points of interest. In every case the

* 'Phil. Trans.,' A, vol. 179 (1888), p. 339.

copper wires showed the cupped formation at the fractured ends. This formation is evidently due to the lower tenacity of the central core, which breaks before the outer skin has completely given way. The skin, therefore, appears like a sleeve pulled over the fractured ends of the core on both pieces. The weakness of the core is caused by the presence of gases, which no doubt originally appeared as bubbles, but which have been drawn out into fine tubes during the wire-drawing. The minute holes dotted all over the broken ends of the core are distinctly visible with a low power objective. From the nature of the fracture it is evident that this fibrous or cellular core is a source of weakness and must considerably reduce the tenacity of the metal. It is possible that the flowing action to which the metal has been subjected may have caused the disengagement of occluded or dissolved gases at the moment of the passage of the *C* into the *A* phase. A proportion of the gas disengaged would naturally be driven in towards the centre of the wire, as the outer skin must be comparatively impervious.

The silver wires occasionally showed a slight cupped formation, but in this case the structure appeared due to the presence of minute bubbles of gas, as if these had been given out at the moment of fracture. In the main the fractured ends present the appearance to be expected from an extremely viscous and fairly homogeneous solid.

The gold wires were practically free from gases, and their fracture was almost perfectly viscous. Fig. 4 is a photograph of the fractured ends of a gold wire, one of which has been slightly etched, to show the stream lines marked out by granules.

GOLD.—Purity, 9997 parts in 10,000. Diameter of wires tested, 0.55 and 0.54 mm.	Tenacity, tons per square inch, at	
	15°.	—182°.
Annealed at 320° and then drawn to 13½ times its original length without further annealing.....	14.6	22.4
Annealed at 320° and then drawn to 3½ times its original length without further annealing.....	15.6	—

In the first test at 15° the wire broke without any general stretching. In the test at —182° there was a general stretch of 11½ per cent., and the diameter was reduced accordingly. The tenacity is therefore calculated on this reduced diameter.

The second test shows that the first wire had been weakened by over-drawing.

SILVER.—Purity, 10,000 parts in 10,000. Diameter of wires tested, 0.55 and 0.46 mm.	Tenacity, tons per square inch, at	
	15°.	—182°.
Annealed at 800° and then drawn to 13½ times its original length without further annealing.....	25.7	34.4
A piece of the same wire further drawn to 1.4 times its length	22.5	—

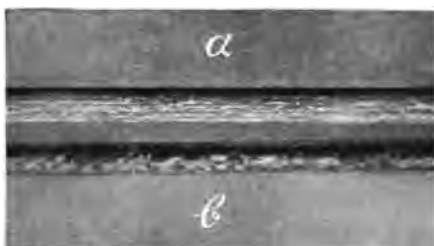
In the first test at 15° the wire broke without any general stretching. In the test at —182° there was a general stretch of 11 per cent. The tenacity was therefore calculated on the reduced diameter. The result of the second test of the further drawn wire makes it probable that the first wire had been over-drawn.

COPPER.—100 per cent. conductivity. Diameter of wires tested, 0.54, 0.46, 0.425, and 0.38 mm.	Tenacity, tons per square inch, at	
	15°.	—182°.
Annealed at 800° and drawn to 5½ times its original length without further annealing. This wire is referred to as (a)	28.4	36
A piece of (a) further drawn to 1.4 times its length	27.1	—
A piece of (a) further drawn to 1.7 times its length	27.4	—
A piece of (a) annealed at 800° and drawn to 1.4 times its length	22.0	—
The same further drawn to 1.7 times its original length	23.7	—
The same further drawn to 2.1 times its original length	25.9	—

In all the tests at 15° the wire broke without any general stretching. In the test at —182° there was a general stretch of 12 per cent. The tenacity was therefore calculated on the reduced diameter.

The further tests show that the full tenacity is not reached by drawing to 2.1 times the original length after annealing. Taken in conjunction with the gold test, however, it would appear that a stretching of three to four times is sufficient to develop the maximum tenacity.

FIG. 1.



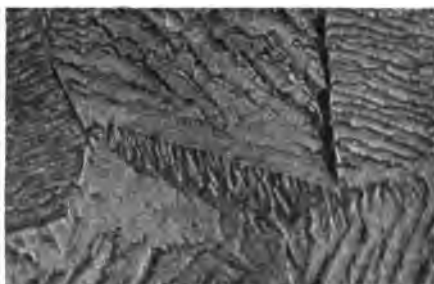
a Surface removed by etching.
b Another piece of same wire annealed before etching.

FIG. 2.



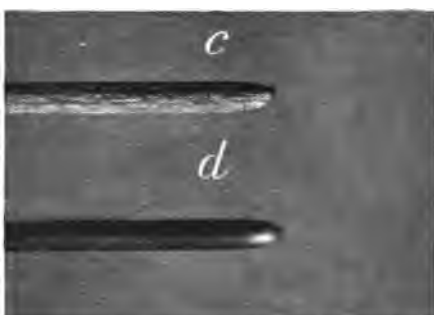
Granular surface of *a*.
Magnification $\times 215$

FIG. 3.



Crystalline surface of *b*.
Magnification $\times 700$.

FIG. 4.



Fractured ends of same wire as *a*.
c Surface removed by etching.
d Natural surface.

Hard-drawn Gold Wire.

The Refractive Indices of Sulphuric Acid at Different Concentrations.

By V. H. VELEY, F.R.S., and J. J. MANLEY, M.A.

(Received March 28,—Read April 6, 1905.)

During the past 60 years various determinations have been published of the refractive indices of sulphuric acid for different concentrations and different rays for the purposes of tracing out the relationships between the refractive energies, dispersion, and chemical constitution. Some observers have published isolated determinations, others more or less connected series, according to the object in view.

Baden Powell* appears to have been the first to give values of the refractive indices of the Fraunhofer lines B, C, D, E, F, G, and H for a sample of acid $d_{18.5/1} = 1.835$ (about 94.5 per cent. concentration), though the temperature of the water density is not given. The object of this work was for the purpose of comparing the observed results for μ_B , etc., with those calculated by Sir W. R. Hamilton's modification of Cauchy's dispersion formula.

Van der Willigen's† investigation remains after the lapse of 36 years the most complete study of the subject; his observations were for 13 Fraunhofer lines, and 17 samples of acid of concentration varying from 0.34 per cent. to 95.61 per cent.; from the results curves are drawn to express the relation of μ and the constants of Cauchy's formula with percentage concentration.

These last were determined by the densities, ascertained by a hydrostatic method and compared with a table of Bineau's construction; subsequently the percentage values have been re-calculated by Pickering‡ and the Kaiserliche Normal-Eichungs Kommission.§

* 'Undulatory Theory as applied to Dispersion of Light,' London, 1841; also 'British Association Report,' 1839, and 'Transactions Ashmolean Society,' vol. 1, 1836.

† 'Archives Musée Teyler,' vol. 1, p. 74, Haarlem, 1868.

‡ 'Journ. Chem. Soc. Trans.,' 1893, vol. 99.

§ 'Wissenschaftliche Abhandlungen der Kaiserlichen Normal-Eichungs Kommission, Part V, Berlin, 1904. Shortly after the present work was commenced, the Directorate of the Commission courteously presented to one of us (V. H. V.) a copy of this report upon the densities and coefficients of expansion of sulphuric acid-water mixtures, together with a recalculation of the values obtained by previous observers. This report has proved of great service to our work; it will be alluded to in the sequel by the abbreviation K.N.E.K., as sanctioned by the usage of the writers of the memoir.

The principal conclusions arrived at by Van der Willigen may be summarised briefly as follows:—

1. Biot and Arago's general formula

$$(100-p)(\mu^2-1)/d+p(\mu'^2-1)/d'=100(\mu''^2-1)/d'',$$

in which p = percentage, μ , μ' , μ'' , d , d' , and d'' are the refractive indices and densities for sulphuric acid, water and the mixtures respectively, is not applicable.

2. The maximum refractive index occurs between the concentrations 81.41 per cent. and 85.98 per cent., corresponding approximately to the monohydrate $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (84.5 per cent.); there are also well-marked alterations in the coefficients B of Cauchy's dispersion formula of the form

$$\mu = A + B/\lambda^2 + C/\lambda^4$$

at about 72 per cent., or the point of maximum contraction of mixtures of sulphuric acid and water.

3. For more dilute solutions an empirical equation $\mu = A + bp + cp^2$ appears to hold good.

Handl and Weiss* gave values of μ for the Fraunhofer lines A, B, C, D, E, and F for sulphuric acid $d\ 20/? = 1.8513$ mixed with successive quantities of water to obtain 9/10, 8/10, etc., concentration. From the densities the percentage values have been recalculated by Gladstone and Hibbert.† The object of their investigation was to trace out the relation between the contraction on admixture and the retardation-coefficient, namely, C/θ , C = contraction, and

$$\theta = \frac{\mu''(V + V_2 + CV_1V_2) - V_1\mu + V_2\mu''}{V_1V_2\mu'\mu''},$$

in which μ , μ' , μ'' have the same significance as above, V_1 and V_2 the volumes of the acid and water respectively, and V that of the mixture.

Gladstone‡ gave the values of μ_A , μ_D , and μ^H for nine samples of sulphuric acid of specific gravity varying from 1.118 to 1.843 (the latter determinations being apparently made at different temperatures), in order to determine the refraction-equivalents of the acid itself.

In a subsequent communication the same author, with Hibbert.§ gives the values for R_A , R_D , R_H , namely, the refractive energies for these three lines for 20 samples of sulphuric acid of percentage concentration varying from 3.25 to 97.5 per cent. Unfortunately only the refractive index for water is given,

* 'Wien. Akad. Ber.,' vol. 30, p. 389, 1858.

† 'Jour. Chem. Soc. Trans.,' 1895, p. 866.

‡ 'Phil. Trans., vol. 160, p. 9, 1870.

§ 'Journ. Chem. Soc. Trans.,' 1895, p. 866.

and not those of the mixtures, nor determinations of the densities, though determined with an error of 1 in 8000, which is fairly large.

It appears that from the original determinations the refractive energies were calculated, that of the water deducted and the remainder taken as that of the acid, a method which, as the authors themselves admit, throws all the errors, whether experimental or arising from impurity, upon the acid. The purport of the argument is to show that the molecular refraction varies but little with the concentration, though subsequently it is shown by a curve that "there is a sudden increase when a little water is added to the anhydrous acid, and after that a slow decrease." The curve given, however, appears to be an abridgment of the curves of Van der Willigen expressed in different terms, and with the errors consequent upon the methods adopted.

It further appears that the method of calculation and reasoning therefrom is at variance with the conclusion of Van der Willigen that a formula such as that proposed by Biot and Arago is unsuitable.

Le Blanc* made seven determinations of the density and μ_D of acids varying in concentration from 4.78 to 94.11, and showed that the values of $M(\mu_D - 1)/d$ for sulphuric acid increases nearly uniformly with the dilution, and from a comparison of these values with those of sodium sulphate, which have a constant value, he infers that the variation in the former case is due to the hydrogen ion with probable exclusion of the sulphion ion.

Hallwachs† gave the ratios of V (dilution as gramme/litre), $V\Delta n \cdot 10^3$ (molecular refraction change), and coefficient of ionisation, and his values show that the two latter increase as the molecular dilution increases.

Pickering‡ recalculated Van der Willigen's results, and gave a rough illustration of the curve of refractive index in terms of percentage concentration, from which it is concluded that the maximum value of the refractive index corresponds with the composition of the monohydrate $H_2SO_4 \cdot H_2O$ (84.5 per cent. H_2SO_4) and there are minor alterations at about 60 per cent., nearly corresponding to the composition of the tetrahydrate $H_2SO_4 \cdot 4H_2O$, and another about 24 per cent. After alluding to possible sources of error in Van der Willigen's determinations, Pickering expresses the opinion that "a full series of observations would supply further important evidence as to the nature of sulphuric acid solutions."

From this *résumé* of literature it appears that the different observers have viewed their results from entirely different standpoints. The recent investigations of Knietzsch§ on the remarkable alteration in the physical and

* 'Zeits. Physikal. Chem.,' (4), p. 533, 1889.

† 'Wied. Ann.,' vol. 47, p. 391, 1892.

‡ 'Jour. Chem. Soc. Trans.,' 1893, p. 99.

§ 'Ber.,' vol. 34, p. 4069, 1901.

chemical properties of sulphuric acid containing 97 to 98 per cent. sulphuric acid, and our own determinations* of the refractive indices of nitric acid induced us to take up the subject with especial reference to the more concentrated solutions, and to the variations, not only of refractive indices, but also of dispersion constants (a subject largely neglected), with percentage strength or molecular dilution.

Determination of Concentration.

The concentration was ascertained by means of the densities, which also serve as factors in the Gladstone-Dale, Lorentz formulæ, and the results at $15^{\circ}/4^{\circ}$ ascertained by Table I of the K.N.E.K. report. Various forms of the U-tube pycnometer were at first tried, but in the case of the more concentrated acids, the risk of absorption of water during the necessary operations appeared to be too considerable. Eventually the capillary bottle pycnometer (of 25 c.c. capacity) was adopted, covered with a glass plate, as used by Mendeleef and Pickering, and weighed against a sealed-up similar bottle as a tare, a very necessary precaution, as pointed out in the K.N.E.K. report p. 216, and more particularly worked out by one of us (J. J. M.).† Each determination was made in duplicate, one with a rising the other with a falling thermometer, the pycnometer being kept in each case in the water bath for about an hour, when it was supposed that the innermost core of acid had attained to the same temperature as the outer portions; the errors of temperature, as recorded by the thermometer, probably did not exceed ± 0.01 . The maximum difference in the two duplicate experiments was about 3 milligrammes for the more concentrated acids, and less for those of lower strength; if the mean value, 1.5 milligrammes, is adopted, an error is implied of 0.0001 in density.

For the thermometer (Gerhardt 5543 Jena glass) ($1^{\circ} = 15$ mm.) used, the following calibrations were undertaken:—(1) Of scale reading by a Hilger travelling microscope, itself calibrated against a metre standard divided into millimetres; (2) of thread-length by Gay-Lussac's method as modified by Thorpe and Rücker‡; (3) of zero displacement; the readings were reduced to the international hydrogen scale by Scheel's tables for Jena glass $16'''$.§ The temperature, as recorded, is thus in accord with that adopted by the K.N.E.K.

The reduction factor for water at 15° was taken from Thiessen, Scheel and

* 'Roy. Soc. Proc.' vol. 69, p. 86, 1901, and 'Phil. Mag.' (6), vol. 3, p. 118, 1902.

† 'Proc. Roy. Soc. Edin.', 1902, p. 358.

‡ 'British Association Report,' 1882, p. 145.

§ 'Wied. Ann.,' vol. 58, p. 168, 1896.

Diesselhorst's* values, and those for reduction of the weighings to vacuum from Kohlrausch's tables.†

As it is not desired to contribute further to the accumulated literature on the densities of sulphuric acid, one example only need be cited to illustrate the degree of concordance of our results with those of previous observers.

The density was determined of a sample of acid supplied by Dr. Messel, purified by frequent crystallisation of the concentrated acid, and similar to those used by W. H. Perkin, sen.,‡ and Pickering§ in their investigations. The value obtained at 15/4 was 1.83736, that calculated by the K.N.E.K. (Report, p. 163) from Perkin's observations at 15/15, 20/20, and 25/25, and reduced to the hydrogen scale is 1.83743, or a difference of 0.00007 in density and of 0.01 in percentage value, namely, 99.62 as against 99.61 per cent.

Determination of Refractive Indices.

The spectrometer, quartz prism with its fittings, and the general methods of observation were precisely as described in our previous work|| on nitric acid solutions, so that it is only necessary to give a brief description and add a few remarks upon the further results of our experience.

The spectrometer, for the continued loan of which we are indebted to the Government Grant Committee of the Royal Society, was obtained from Becker (Meyerstein's successor). Its graduated circle is 27 cm. diameter, and reads directly to $1/10^\circ$; it is furnished with two reading microscopes, supplied with micrometers, three revolutions of which correspond to one scale-division; as the micrometer screw heads are divided into 60 parts, an observer is enabled to read directly to two seconds. The circle was calibrated by both the telescope and plumb-line methods, which we have described.¶ The dimensions of the plates of the quartz prisms were 75 mm. \times 68 mm. \times 6 mm., of the aperture 20 mm., and the angle of the prism about $60^\circ 6'$. The plates were cemented on by paraffin, purified by sulphuric acid, and then frequently by water; it did not appear that any subsequent action between the acid and the paraffin occurred in the course of the observations.

It was found that vibrations due to traction engines, wagons, etc., passing

* 'Wied. Ann.,' vol. 60, p. 340, 1897.

† 'Leitfaden,' p. 408.

‡ 'Journ. Chem. Soc. Trans.,' 1886, p. 782.

§ 'Journ. Chem. Soc. Trans.,' 1890, p. 73.

|| Cf. reference (p. 472).

¶ Drude's 'Annalen der Physik,' vol. 4, p. 575, 1901.

along the street, situated some 35 yards from the laboratory, might produce a variation in reading of as much as 20'' of arc; these vibrations doubtless caused some displacement of adjusting screws or springs. The errors arising from these variations were duly corrected.

The angle of the prism was found to vary about 10'' in different rebuildings, sometimes in one and sometimes in the other direction; its value was, therefore, taken every few days. The two extreme values were 60° 6' 0'' and 60° 6' 24''.

As in our previous work the minimum deviation was determined at three different temperatures; from the values obtained the coefficient of variation per degree temperature was calculated out, and from its mean value the minimum deviation at 15° was estimated, and this used for the recorded value of μ . One series of observations will serve to illustrate this adopted method.

Concentration of sample, 85.92°. Line D.—

(a) Minimum deviation	32° 6' 42'' at 13.6
(b) " "	32 4 2 15.5
(c) " "	32 11 22 10.1

Variation of minimum deviation per degree temperature (K)—

From (a) and (b)	K = 84''
(a) (c)	K = 80
(b) (c)	K = 82
Mean.....	82''

Using the above variation, the corrected values for minimum deviation at 15 appear as under—

(a) 32° 4' 51''	} Mean value	32° 4' 47''
(b) 32 4 47		
(c) 32 4 44		

Value of μ_{15}^D calculated from above = 1.438632.

In some of the later experiments the above method was slightly modified as follows: observations were made at every 1/5° through one whole degree with the thermometer rising very slowly; from these the mean value of the minimum deviation at the mean temperature was calculated. The temperature was then raised slowly about 2°, and a second series of observations made at every 1/5°, which were dealt with similarly. Finally, the two sets of observations were compounded together, and their mean taken at mean temperature; the value thus obtained was the result of 10 distinct determinations.

Spectrum Lines Used.

The sodium line and the three hydrogen lines H_{α} , H_{β} , and H_{γ} , were used for the determinations; the first was obtained by a flame, and the three last from two Pflücker tubes of slightly varied construction. It was found after several attempts that the line H_{β} was not practicable to deal with, a result in accordance with observations of other workers upon refractive indices. The wave-lengths of the four lines used were taken as 589.3 (mean of D_1 and D_2), 656.3, 486.1, and 434 millionths millimetre respectively.

Magnitude of Error.

Adopting all the corrections detailed in the present and previous communication, we believe that the errors in the values of μ do not exceed a few units in the sixth places of decimals for acids below 90 per cent. concentration; above this the error may amount to one unit in the fifth place. At present one of us (J. J. M.) is engaged upon devising a method of overcoming the experimental difficulties in dealing with acids of the highest concentration.

Samples of Sulphuric Acid.

We are indebted to Dr. Messel for a liberal supply of two samples of acid (both of which had been purified by frequent crystallisation), one labelled *concentrated* acid and stated to be of 99.7 per cent. strength, the other labelled *catalytic* acid, and stated to be of 99.5 per strength. The values found by us by the densities at 15/4 according to the K.N.E.K. tables were 99.62 and 99.4 respectively; these slight differences are within the errors of observation. The values found for μ and d for these two acids were compared at nearly the same concentration, 76.31 and 76.59 respectively; they differed only so far as the differences of concentration. These acids may, therefore, be taken as identical in physical properties, though their past history of manufacture was different.

A third sample, used for one determination only in the present work, was purchased of Herr E. Merck, of Darmstadt, as of 1.84 density; the value found at 15/4 was 1.84161, which is slightly higher than the maximum 1.84148, found by the K.N.E.K. at 97.3 per cent. The difference, 0.00013, corresponds to error in weighing of the acid of 2 milligrammes, or a difference of temperature of about 0.11.

Certain tests were made to ascertain the purity of the several samples of acid as follows:—

1. *Organic matter* and *sulphurous* acid 0.1 c.c. permanganate solution (containing 0.1 milligramme available oxygen) added to 10 c.c. acid and 20 c.c. water. Catalytic acid, trace of these impurities, concentrated and Merck's acid. free.

Chlorine by dilute silver nitrate solution added to acids diluted as above. Concentrated acid, minute trace, catalytic and Merck's acid free.

Nitric Acid.—By addition of diluted acids to a crystal of brucine, all acids free.

Nitrous Acid.—By the meta-phenylene diamine test, which according to our previous investigations will reveal the presence of 1 part in 15×10^7 of this impurity. Concentrated and catalytic acids at limit of delicacy, Merck's acid beyond the limit.

Ammonia.—An excess of soda solution free from ammonia was added to 10 c.c. of each sample of acid, and then 2 c.c. of Nessler's solution added. A faint yellow tint was produced in the case of all three acids, indicating a slight trace of ammonia, which would produce no effect on the results.

Purification of Water used for Dilution.

Ordinary tap water was boiled for some time in an open copper boiler to drive off dissolved gases and other volatile matter; the boiler was then closed and the steam passed into two boiling dilute solutions of potassium permanganate (the first slightly acidified, with sulphuric acid, the second, strongly alkaline), which were contained in bolt-head Jena glass flasks of about 1 litre capacity. The steam then passed through a form of spray tap, which proved highly efficient, and thence into a condenser with a block-tin inner tube; the water dripped into a bottle, invariably steamed out previous to use. Though rubber stoppers were used in the apparatus, yet it was found that if these had been well steamed previously, no sensible amount of impurity was imparted to the water.

The specific conductivity $\text{Kcm}^{-1} \text{ohm}^{-1}$ of numerous samples of this water was determined as a test of purity; it varied from 1.2×10^{-6} to 1.5×10^{-6} . The former value does not differ widely from that (0.96×10^{-6}) found by Kohlrausch and Maltby* for water specially purified, but not distilled in vacuum, which last has a value of 0.04×10^{-6} . The above investigators from the observations of Knox† have traced the difference to dissolved carbon dioxide. Adopting the data of the latter, the molecular proportion of carbon dioxide in our samples of water would vary from 0.000057 to 0.000081 gramme equivalent litre, or a quantity which can with all reason be assumed to be insufficient to produce any sensible difference in the determinations of refractive index.

The value found for water prepared according to the method described above was $\mu_D^{15} = 1.333468$; as this is lower than the value found by others,

* 'Wiss. Abh. Reichsanstalt,' vol. 3, p. 193, 1900.

† 'Wied. Ann.,' vol. 54, p. 54, 1895.

as also by ourselves in our former work, it was thought desirable to repeat the observations, and the results are briefly tabulated as under:—

Water. Mean conductivity, $K = 1.3 \times 10^{-6}$.

Temperature.	No. of observations.	δ_{15} (reduced).
19.2	4	23° 40' 57"
14.8	4	23 40 59
14	3	23 40 59
14.5	1	23 40 57
15.1	4	23 40 56

The mean value of the 16 observations is $\delta_{15} = 23^\circ 40' 58'' \pm 0.23''$; the refracting angle of the prism, rebuilt for the purpose, was $60^\circ 6' 20''$; hence $\mu_D^{15} = 1.333393$, still slightly lower.

In order to determine whether the discrepancy was due to dissolved carbon dioxide, in however small a proportion, or to dissolved silica, the following series of experiments were conducted.

Firstly, as to carbon dioxide, the gas was prepared from marble and dilute hydrochloric acid, both of reasonable purity; it was washed with water and then passed through a tube about $\frac{1}{2}$ metre long, packed with marble, the further end of which was drawn out and bent round, so that the gas might be delivered into the water contained in the prism and impurity due to rubber connections avoided.

To ascertain the efficacy of the apparatus for the purpose required, the packed tube was first steamed out and then the gas passed into water to the point of saturation. The solution thus obtained was free from all trace of hydrochloric acid.

The results of the observations upon the effect produced by the solution of the carbon dioxide are given below:—

No. of experiment.	μ_D^{15} .	Remarks.
I	1.333386	Volume of gas dissolved about 1.5 c.c.
II	1.333371	„ „ 3.0 c.c.
III	1.333335	Water saturated.
IIIA.....	1.333365	Solution III after standing for 13 hours.

It is evident from these results that the presence of carbon dioxide decreases the refractive index of water, and the greater the amount so dissolved the lower the value, and conversely, if the gas passes out of solution the value is increased.

Secondly, as to silica; a crystal of quartz was boiled in nitro-hydrochloric

acid, then with highly purified water; it was then ignited and quickly dropped into water; the powder thus obtained was frequently washed.

The results of the observations are given below :—

Value of μ_D^{15} for a freshly prepared sample of water = 1.333393.

„ „ left in contact with quartz for 13 hours = 1.333371.

The presence of silica also reduces the value of the refractive index, though only to a degree almost inappreciable. So far as we are aware there has been no investigation upon the solubility of silica in water as determined by the method of electric conductivity.

The case of the discrepancy between the value of the refractive index as found by ourselves and previous observers may be summarised as follows :—

Our lower value might, so far as the observations upon the effect produced by carbon dioxide indicate, be due to that cause, but, on the other hand, the frequently repeated determinations of the electric conductivity show that the amount of this impurity present was insignificant, being not greater than that found by other workers for samples of water carefully rectified, but not distilled in vacuo. The lower value might also be due to silica, though the alteration produced by this substance is very slight even in extreme circumstances.

On the other hand the higher value found by previous observers might be due to the solution of alkalies and other metallic oxides from the glass used for the prisms.

It would require a prolonged series of experiments to decide this matter, and as the refractive index of pure water is only incidental, so far as regards the present investigation, we prefer only to state the case and to leave it as a subject of further enquiry.

Results.

In the following table are given in Column I the reference number of sample, in Column II the percentage value as deduced from the density, and in Columns III–VI the values of μ reduced to 15° C. for the four lines H_α , D, H_β and H_γ respectively.

Table I.

I.	II.	III.	IV.	V.	VI.
1	0·84	1·332805	1·334664	1·338807	1·342029
2	1·76	333944	335794	339994	343181
3	3·88	336416	338313	34249	345704
4	5·1	337896	339355	343964	347326
5	9·58	343485	345361	346633	352955
6	14·0	349001	350953	355233	358576
7	18·31	354322	356297	360653	363939
8	22·16	359194	361248	365598	368854
9	25·9	364051	36605	370506	373882
10	29·24	36811	370196	374726	378211
11	30·86	370161	372280	37683	380248
12	34·35	374213	376332	380948	384426
13	38·48	379184	381388	386002	389530
14	42·45	384119	38635	39099	394507
15	46·46	388987	391184	395934	399508
16	52·24	393336	395589	403405	406851
17	56·22	401655	403907	406767	412274
18	59·65	406267	408582	413445	416976
19	62·88	410536	41285	417767	421437
20	66·44	415487	417822	422782	426452
21	69·6	419838	422156	427177	430848
22	72·28	423549	42595	430943	434584
23	74·86	426858	429185	434234	437933
24	76·3	429767	431132	436185	439887
24(bis)	76·59	42903	431398	436494	440167
25	78·09	430641	433208	438242	441988
26	80·05	432946	43529	440335	444079
27	80·43	43323	435628	440658	44438
28	81·77	434442	436818	441871	445582
29	83·2	435459	43782	442875	44657
30	84·56	436051	438403	443417	447071
31	85·50	436267	438632	443603	447277
32	85·92	436272	438632	443651	447384
33	86·37	436246	438591	44367	447324
34	87·40	436065	43841	44341	447031
35	90·53	43418	436468	441361	446978
36	95·33	430662	439061	437836	441402
37	97·3	425367	427482	432064	435420
38	98·7	41947	421558	426025	429396
39	99·3	418387	420450	429845	428206

We give by way of comparison the results obtained by Van der Willigen* and ourselves for four acids of approximately the same concentration. The former have been reduced as to densities to the hydrogen scale, and as to percentages to modern atomic weights by the K.N.E.K., and to a temperature of 15° by the temperature coefficients found by ourselves.

The agreement, having regard to the large number of corrections involved and to the difference of purity of water and acid, is for the most part satisfactory except for H₇. The diversity in the last case may arise either from differences of method, Van der Willigen using a heliostat of the Fahrenheit type and a 1/100-inch grating, as against our Pflücker tube, or to

* *Loc. cit. supra.*

Table II.

	V. d. W. 88.63 per cent.	V. and M. 88.47 per cent. (88.63 corr.).	Diff.	V. d. W. 56.23 per cent.	V. and M. 56.22 per cent.	Diff.
H _a	1.37984	1.37937	+47	1.40185	1.40166	+19
D	38113	38158	+45	40419	40391	+28
H _b	38678	38619	+59	40688	40677	+11
H _c	39054	38972	+82	41257	41227	+30
	72.14 per cent.	72.28 per cent.		81.68 per cent.	81.77 per cent.	
H _a	1.42315	1.42336	-21	1.43453	1.43444	+9
D	42565	42575	-10	43695	43682	+13
H _b	43067	43074	-7	44195	44188	+7
H _c	43472	43438	+34	44605	44558	+47

the angle $34^{\circ} 15'$ of the prism used by the former, which, as he himself admits, was smaller than desirable, or to both causes combined.

Temperature Coefficients.

The values, up to the concentration 22.16, expressed in terms of 10^{-6} and calculated as explained above, are given below:—

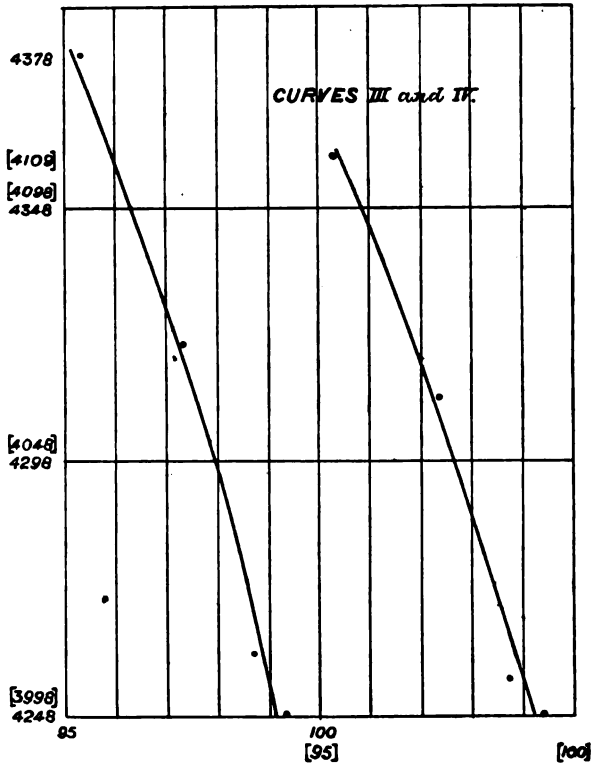
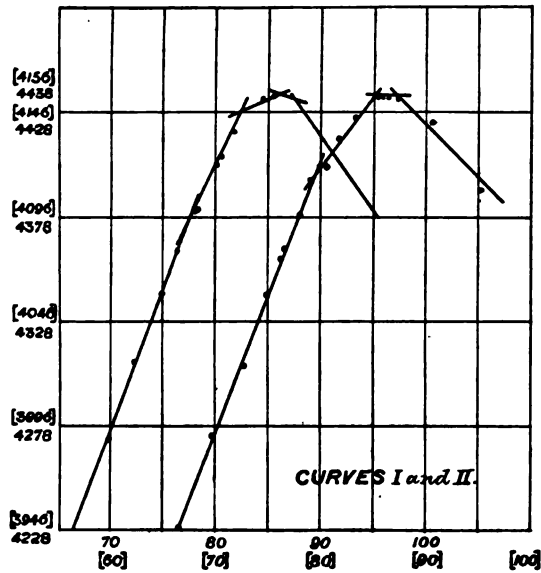
Table III.

Concentration.	Temperature coefficient.	Concentration.	Temperature coefficient.
0.84	86	9.58	150
1.76	101	14.0	170
3.88	101	18.31	213
5.1	180	22.16	256

The coefficients beyond this point are practically constant within the limits of experimental error, with a slight maximum between the concentrations 84–87 per cent., from which there is a tendency towards a minimum.

It will be evident from the data given in Tables I and III that the refractive indices increase uniformly up to a concentration of about 76 per cent., thence more gradually to the maximum point at or about 85.5 per cent.

The values of μ for H_B and A_D (the latter being shifted 10 units along the abscissæ axis to the right to avoid too much overlapping), in terms of percentages from 66 to 94 per cent., are illustrated in Curves I and II, from which it is manifest that these values may be represented as linear functions of the percentages, though it is possible that about the maximum point the



results might be represented upon a curve to which the straight lines depicted are tangential. Curves III and IV (on a more open scale) illustrate

the results from 94 to 100 per cent. in like manner; these show a distinct curvature, probably of a hyperbolic type.

The most definite, namely, the maximum point, corresponds approximately with the composition of the hydrate $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (84.48 per cent.), though slightly above it, as previously observed by Van der Willigen.* Less marked points occur at about 76 for μ and at 66 per cent. for Cauchy's constant B, which again correspond only approximately with the hydrates $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (73.13 per cent.) and $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ (64.47 per cent.). As we have pointed out in a previous communication,† the points of discontinuity are to some extent ideal, in that an apparently abrupt change of events can be resolved into a gradual transition stage. It is not our purpose to deal further with the question of the existence or non-existence of hydrates in solution, as it has been so fully and fairly discussed, and the literature thereon so carefully collated by Drs. Domke and Bein‡ quite recently, that any further remarks on our part would be superfluous.

The irregularities observed from 95 to 100 per cent. will be considered in a subsequent section.

Refraction Equivalents.

As mentioned above, the molecular refraction equivalents of the sulphuric acid as the differences between those of the several solutions and the water contained therein have been calculated by Gladstone and Hibbert§ according to the factor of the former $(\mu - 1)/d = \text{constant}$.

But, on the one hand, such a method of treatment does not appear to us to be reasonable, and on the other the factor is only empirical. Though we have calculated out the values of $(\mu_D - 1)/d \cdot 10^{-5}$ for the various solutions, and found that they decrease approximately as a linear function of the concentration, yet we refrain from giving these data, as less satisfactory than those obtained by using the more rational factor of Lorentz.

In Table IV are given respectively in Column 1 the concentrations, in Column 2 the calculated values for $(\mu_{\text{H}_2\text{O}}^2 - 1)(\mu_{\text{H}_2\text{O}}^2 + 2)d$ (hereafter designated $R_{\text{H}_2\text{O}}$, etc., for the sake of brevity).

The values of the factor $\Delta R/\Delta p$ up to a concentration of 90 per cent. vary only by one or two units from 70, having regard to errors of experiment.

This relation, $\Delta R/\Delta p = \text{constant}$ may be put into the form of an equation

$$R_1 = R - a\Delta p,$$

* *Loc. cit. supra.*

† 'Roy. Soc. Proc.,' vol. 69, p. 119, 1901.

‡ Cf. reference above; 'Zeits. Anorgan. Chem.,' vol. 43, pp. 153 to 155 and 178 to 181, 1905.

§ *Loc. cit. supra.*

Table IV.

Concentration.	R _{Ha} .	Concentration.	R _{Ha} .	Concentration.	R _{Ha} .
0·84	20452	38·48	17887	78·09	15129
1·76	20390	42·45	17605	80·43	14970
3·88	20245	46·46	17325	81·77	14877
5·1	20160	52·24	16918	83·2	14781
9·58	19862	56·22	16642	84·56	14694
14·0	19561	59·65	16400	85·92	14598
18·31	19265	62·88	16169	87·4	14500
22·16	19003	66·44	15936	90·53	14294
25·9	18752	69·6	15708	95·33	14037
29·24	18516	72·28	15527	97·3	13895
30·86	18408	74·86	15347	98·7	13738
34·35	18160	76·3	15241	99·3	13715

in which R is the value for any concentration taken as an origin of co-ordinates, and a the constant. But a closer inspection of figures and the calculation of data from the above equation show that there is a slight alteration at about 30 per cent., not amounting to more than 1·5 per cent. in the factor. It is not desired to lay too much stress upon this change, which is of the nature of a very gradual transition, but merely to mention that this is the point of maximum electric conductivity as observed by Kohlrausch* and others, and also a point of variation in the factors of other physical properties.

Otherwise the evidence is against the existence of hydrates or, to put the case in another form, it matters not whether the water is combined either with the sulphuric anhydride or the sulphuric acid, or combined with neither.

The exceptional values of $\Delta R/\Delta p$ for the four several lines for the higher concentrations are given below :—

Table V.

Concentration.	H _a .	D.	H _p .	H _r .
90·53	66	69	69	67
95·33	53	46	50	51
97·3	71	90	90	87
98·7	112	115	115	113
99·3	38	33	35	36

In the succeeding table the differences, in terms of 10^{-5} , are given between the values of the Lorentz equivalent observed, and those calculated from the general formula $R_1 = R - a \Delta p$, the two lines selected being D and H_r , namely, the most and least practicable for observation purposes.

* 'Pogg. Ann.' vol. 138, pp. 238, 370, 1869; *ibid.*, vol. 151, p. 378, 1874, etc.

For the D line $\alpha = 68.5$, $R = 20,348$ between the limit 3.9 and 29.2 per cent., and $\alpha = 68.9$, $R = 18,501$, between the limits 30.8 and 90.5 per cent.; similarly, for the H _{γ} line, $\alpha = 70.5$, $R = 20,963$, between 0.9 and 29.2 per cent., and $\alpha = 72$, $R = 18,869$, between 30.8 and 90.5 per cent.

The greatest difference between the observed and calculated results amounts in one case only to 40 in 14,000, but in the large majority of cases to less than one-fourth of this, which is within the limits of experimental error.

In Curve V the percentages are given along the abscissæ axis, and the values of the Lorentz factors (to four places) as ordinates; the former are for the purpose of abbreviation divided into three sections, namely, from 0 to 30, 30 to 60, and 60 to 92 per cent. respectively.

Table VI.

Percentage.	Difference.		Percentage.	Difference.	
	D.	H _{γ} .		D.	H _{γ} .
0.84	—	—	62.88	-19	-19
1.76	—	- 3	66.44	-20	-14
3.88	—	- 9	69.6	-15	-11
5.1	+ 3	0	72.28	- 7	+ 5
9.58	- 6	+ 1	74.86	-11	+ 1
14.0	- 7	+ 1	76.3	-28	-14
18.31	+ 1	- 5	78.09	+ 9	+13
22.16	+ 6	0	80.06	+21	+ 6
25.9	+ 3	+ 5	80.43	- 3	+ 4
29.24	0	+ 4	81.77	0	+11
30.86	—	—	83.2	+ 3	+13
34.35	- 6	-13	84.56	+ 3	+ 8
38.48	+ 6	0	85.5	+12	-16
42.45	+ 5	- 6	85.92	+ 8	+18
46.46	-10	+24	86.37	+ 8	+18
52.24	- 7	-10	87.40	+11	+12
56.22	-12	-12	90.53	+22	+40
59.65	-12	-24			

These results are in general accordance with those which we obtained in the case of nitric acid, the only points of difference being the value of the constant, namely $70 \cdot 10^{-5}$ instead of $(40 \text{ to } 50) 10^{-5}$, and the fewer transition stages. It is possible that the difference of the factor is mainly due to the presence of a second hydroxyl grouping, more especially as recent investigations* upon dielectric constants (K) have shown that the presence of such hydroxyl groupings increase the value beyond that required for the right hand side of the original equations of Lorentz,

$$(\mu^2 - 1)/(\mu^2 + 2)d \quad \text{and} \quad (K - 1)/(K + 2)d \quad \text{each constant.}$$

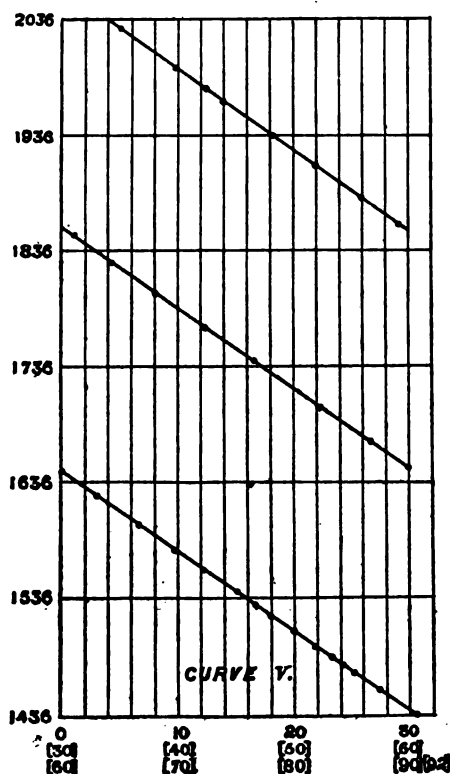
* Thwing, 'Zeits. Physikal. Chem.,' vol. 14, p. 286, 1894.

Unfortunately neither the observations at present accumulated* nor the degree of accuracy desirable are sufficient to determine whether an equation of the form

$$(K' - 1)/(K' + 2)d = (K - 1)/(K + 2)d - a\Delta p$$

would hold good.

However this may be, if we consider the concentrations from 3 to 95 per cent., though the density according to the various memoirs on the subject



is a very complicated function of such concentrations, yet the factor $(\mu^2 - 1)/(\mu^2 + 2)$ is a linear function of the density, or in other words the ethereal elasticity is in simple direct relation to the density,† rather simpler in the case of sulphuric than of nitric acid.

It is, of course, true that the range is very short, namely from $\lambda = 434 m\mu$ to $\lambda = 656.3 m\mu$, approximately that of a major fifth in a musical scale, but restrictions are imposed by the limits of human vision and the particular

* Fleming and Dewar, 'Roy. Soc. Proc.' vol. 61, p. 309, 1897, and vol. 62, p. 258, 1898.

† Cf. Larmor, 'Phil. Trans.,' A, 1897, pp. 236 to 246.

method of experiment. The discrepancies for the ranges 0 to 3 per cent. and 95 to 100 per cent. are doubtless due to wholly different causes.

Similarly our observations show a sudden fall in the factors $\Delta_{\mu\beta}/\Delta p$ and $\Delta A/\Delta p$ at 97.3 per cent., proceeding to 98.7 per cent., followed by a rise at 99.3 per cent., namely, the curves for these factors and of density in terms of percentage are parallel.

Conversely for the factors $\Delta R/\Delta p$, commencing with a change at 95 per cent. there is an increase from this point up to 98 per cent., followed by a fall, or the curve for $\Delta R/\Delta p$ in terms of p is the curve for d in terms of p inverted.

The constitution of sulphuric acid about 100 per cent. H_2SO_4 has recently been discussed by Domke and Bein,* and the conclusion arrived at is to the effect that there is no simple substance of the composition represented by the formula H_2SO_4 (however convenient such an ideal substance may be for the purposes of computation), but that it is a mixture of molecules H_2SO_4 , SO_3 and H_2O or $H_3SO_3SO_3$, or it may even contain pyrosulphuric acid $H_2S_2O_7$. In our former communication on the electric conductivity of nitric acid† from the irregularities observed we put forward the similar view that the substance represented by the formula HNO_3 is also an ideal, and that it is a mixture of HNO_3 , N_2O_5 , and H_2O .

It is to us a source of gratification to find ourselves so completely in accord with our fellow workers in another country, even in giving up familiar and possibly cherished notions.

Summary.

1. The refractive indices of sulphuric acid-water mixtures of concentration varying from rather under 1 per cent. to rather over 99 per cent. have been determined for the four lines H_α , D , H , H_γ , and the results compared in certain cases with the previous observations of van der Willigen.

2. The temperature coefficients, within practicable limits, have been measured, and these values used for reducing all the refractive indices to a common temperature of 15.

3. The maximum value of the refractive indices and of the first constant of Cauchy's formula occur at a point which corresponds approximately with the composition of the hydrate $H_2SO_4 \cdot H_2O$, but otherwise any indication of the existence of other hydrates is doubtful.

4. Lorentz's factor, $(\mu^2 - 1)/(\mu^2 + 2)d$, is a linear function of the percentage up to 90 per cent., or in other words the ethereal elasticity is compensated by

* *Loc. cit. supra.*

† 'Phil. Trans.,' A, 1898, p. 365,

the density. There is, however, a slight alteration at about 30 per cent. concentration. The differences are given between the calculated and observed values for this factor as from an equation $R' = R - a \Delta p$ in the case of the lines D and H_γ.

5. The refractive indices, the Cauchy constants and the Lorentz factor all show irregularities for concentrations 92 to 100 per cent., which are consistent among themselves, as also with a maximum density at about 97 per cent., and a minimum point between 99 and 100 per cent.

The question is, therefore, again raised as to whether a substance represented by a simple formula H₂SO₄ does exist as a distinct entity, and a comparison is drawn herewith between nitric and sulphuric acids.

6. As an incidental point the effect of carbon dioxide and of silica upon the refractive index of water is discussed, but the final interpretation of the results left as a subject of further enquiry.

In conclusion we desire to express our obligations to the Kaiserliche Normal-Eichungs Kommission for sending their publications and the kindly interest which they have taken in our investigations, to Professors Elliott and Esson, to Dr. Messel, Mr. James Walker, and others who have rendered us assistance in matters of difficulty.

On the Spectrum of the Spontaneous Luminous Radiation of Radium. Part III.—Radiation in Hydrogen.

By Sir WILLIAM HUGGINS, K.C.B., O.M., D.C.L., Pres. R.S., and
Lady HUGGINS, Hon. Mem. R.A.S.

(Received August 24, 1905.)

As soon as we found* that the glow of radium bromide consisted mainly of light from nitrogen stimulated into luminosity by the radium, and giving the negative pole spectrum, we formed the intention of photographing the spectrum of the glow when the radium bromide was placed in an atmosphere of hydrogen, primarily in the hope of finding an answer to the question raised in our first paper, "Have we to do with occluded or with atmospheric nitrogen?"†, and, in the second place, to determine whether the radium is able to render hydrogen luminous.

In these experiments some unexpected results came out, which made it desirable to repeat them many times. This circumstance, together with the long exposures necessary—from 10 to 14 days—and the slow changes which we found to take place in the radium when allowed to remain in the hydrogen for long periods, reckoned in months, have necessarily delayed the publication of this paper. The investigation is still in progress, but it seems desirable not to delay any longer the publication of the results which have been already obtained.

An account of each experiment would make the paper long and unnecessarily tedious. It will be sufficient to give the results of each group of experiments made under similar conditions. The same form of apparatus was used for all the experiments. Small glass vessels were prepared consisting of a round cell with flat base, to hold the radium, into which, on opposite sides, tubes of small bore were blown, the walls of the cell were ground flat on the top to receive a thin microscopic cover-glass, or a thin plate of quartz, which was cemented down after the radium salt had been placed on an ebonite support within the cell.

As the glow of radium takes place at atmospheric pressure, it was desirable that experiments with hydrogen should be made under like conditions. A current of hydrogen was allowed to flow through the glass vessel for some minutes until all traces of air must have been carried out; the two tubes

* 'Roy. Soc. Proc.,' vol. 72, pp. 196 and 409.

† *Ibid.*, p. 199.

were then sealed up, leaving the radium in hydrogen at atmospheric pressure.

Afterwards, a second series of experiments was made with hydrogen at reduced pressure. The glass vessel was connected with a vacuum pump and exhausted to below 1 mm. of mercury; hydrogen was then allowed to enter. The vessel was again exhausted and refilled with hydrogen several times, and was then sealed up with the contained hydrogen at the pressure of about 1 mm. of mercury.

Portions of the same two specimens of radium bromide which had been used in our former experiments were employed, namely, one from Buchler & Co., Brunswick, and the other from the Société Centrale de Produits Chimiques, Paris.

The results of repeated experiments made in hydrogen at atmospheric, and also at reduced, pressure, and with both samples of radium bromide, were uniformly similar. The glow became sensibly fainter to the eye when the radium had remained for a few days in hydrogen; perhaps the diminution of the brightness took place sooner in hydrogen at reduced pressure. Photographic plates, exposed in the spectroscope to radium in hydrogen for the same time as to the same radium in air, showed a feebler spectrum, which was that of nitrogen without any traces of the lines of hydrogen.

From these experiments we may assume either the existence of occluded or combined nitrogen, or that the spectrum was due to minute traces of air which had remained within the vessel. If, however, the increasing feebleness of the glow was due to the latter cause, we should expect that on unsealing the tubes and admitting air, the glow would at once recover its original brightness. On April 15, 1904, when the radium had remained 26 days immersed in hydrogen, the tubes were opened and air blown through, but no recovery of brightness as estimated by the eye took place at the time. Then a photographic plate was exposed in the spectroscope for seven days, on which, when developed, the nitrogen spectrum was even feebler than on a similar plate which had been exposed for the same time before the air was admitted. A few days later, however, a small increase of brightness was detected by the eye, which continued until the radium slowly recovered its original brightness.

When radium was allowed to remain for months in an atmosphere of hydrogen some unlooked-for results were observed.

Experiment 1.—A portion of the Brunswick radium bromide was sealed up in hydrogen at reduced pressure on June 24, 1904.

(a) As in former experiments, the brightness of the radium bromide, as estimated by eye, gradually diminished.

(b) Photographs taken with the spectroscope showed the nitrogen spectrum only, and with increasing feebleness as time went on, until the strongest of the nitrogen bands only were just suspected upon the plate.

(c) Some days after sealing up in hydrogen, the radium bromide, which was originally of a yellowish-cream colour, began slowly to become darker, until by August 9, 1904, it had reached a dark russet brown.

(d) On March 17, 1905, the radium, which had now been sealed up for nearly eight months, was observed by eye to have become much brighter, indeed nearly as bright as the French radium which had remained in air. Unfortunately the radium in the hydrogen had slipped out of the ebonite support to the bottom of the cell, and, therefore, could not be brought before the slit of the spectroscope. It was then decided to open the vessel and remove the radium in order to photograph its spectrum while in this brighter condition. Before placing it in the spectroscope it was thought desirable to compare it again at night, about eight hours after it was taken out of hydrogen, with radium which had remained in air. To our great surprise the radium removed from the hydrogen had completely lost its light, it was now quite dark, without any sensible glow. It retained its very dark russet brown colour.

(e) Before the vessel was opened, while the radium was bright in hydrogen its radio-active power was measured with an electroscope; after it had been removed from the hydrogen and had become dark and glowless, its radio-activity was again measured. The amount of the induced leak of the charged leaves was found to be the same as before, showing that the sudden change from a bright condition to one without any sensible glow had not been accompanied by an alteration in the intensity of the β - and γ -rays.

(f) The glowless radium was examined in the dark at intervals of a few days. By May 9, 1905, a very faint glowing was perceived, and at the same time the dark brown colour was observed to have become less intense. These changes proceeded slowly until, by August 13, the radium had regained its original creamy colour and nearly its original brightness. During these three months its radiation, as measured by the electroscope, remained the same.

Experiment 2.—Fortunately we have for the purpose of comparison a portion of the French radium which has been sealed up in hydrogen at reduced pressure since September 12, 1904, about 11 months. Many photographs of the spectrum of this sealed-up radium have been taken at intervals from last September to the present time, showing, with similar exposures, increasing feebleness, but always, when any action could be detected upon the plate, some of the stronger bands of the nitrogen spectrum. Recently,

however, a band has appeared in the green part of the spectrum, for which the plate is but feebly sensitive, without any action being discernible on the plate in the blue and violet regions, for which the photographic film is greatly more sensitive. Fortunately on one plate the chief bands of the nitrogen spectrum, though excessively faint, can be just detected, while at the same time the new band, falling in a much less sensitive region photographically, is relatively strong.

The defined line which begins the band on the less refrangible side is a little more refrangible than the brighter edge of the green band of the Swan spectrum at λ 5165. The band has not yet been identified.

The band is accompanied by a faint continuous spectrum which runs back to D.

The radium bromide has turned to a dark russet brown colour, as in the former experiment. To the eye the brightness of the radium has remained greatly diminished, until within the last few days, when we suspect that, as in the preceding experiment, a slow increase of brightness has set in.

On re-examining all the photographs of the spectrum of the glow of radium which we have taken, a plate was found, developed on August 23, 1904, of the spectrum of a portion of the French radium which had been sealed up in hydrogen for a few days only, but when its light had faded to about one-half, which shows very faintly, but unmistakably, the new band.

The suggestion presents itself to the mind whether in both experiments when the radium had almost ceased to glow with nitrogen light, it was able to stimulate the molecules of the substance producing the band into luminescence. On this supposition an explanation of the sudden going out of the bright glow when the radium was taken out of the atmosphere of hydrogen in the first experiment would be found in the absence in the atmosphere of the needful molecules, the radium having lost temporarily the power of exciting nitrogen, unless we take the view that, to be stimulated into luminescence, nitrogen must be not merely in outward contact with the radium, but in a more intimate connection with it, which time is required to bring about.

The suggestion was considered in a former paper whether the operative cause of the glow was to be found in the β -rays, which are known to be analogous to the cathode corpuscles, upon the nitrogen of the air. In these recent experiments the electroscope showed that these rays, and the γ -rays, were being radiated with undiminished force at the time that the radium bromide remained glowless in air. It may be mentioned here that the cathode discharge is efficient in bringing out easily the first spectrum of

hydrogen,* but the radiations of radium appear to be unable to do this. Our experiments seem rather to support the view, suggested in our first paper, that the spontaneous light of radium may not be produced by any form of its radiations acting upon the nitrogen of the air outside it, but by a more direct action through encounters with nitrogen molecules, in some way associated with the radium, of those molecules of the radium which are undergoing active changes.

The Pressure of Explosions.—Experiments on Solid and Gaseous Explosives.

By J. E. PETAVEL.

(Communicated by Arthur Schuster, F.R.S. Received August 18, 1905.)

(Abstract.)

Although this subject has been dealt with by numerous investigators, certain branches of it still remain practically untouched. With regard to the solid explosives used in ballistic work, the maximum pressure developed is usually well known, but the conditions which govern the combustion of the charge and the rate of cooling of the gaseous products require further investigation.

Explosive gaseous mixtures have only been studied at initial pressures but little above that of the atmosphere. Even in the case of coal-gas and air, which forms an exception to this rule, the work has not been extended to high pressures. The present research was undertaken with a view to filling in these gaps.

The first part of the paper describes the apparatus which was used for the investigation of both solid and gaseous explosives; the second part deals specially with the properties of cordite. The pressures are photographically recorded on a revolving cylinder by means of a specially constructed manometer. This manometer was designed with the object of securing the lowest possible time period.

The rise of pressure during the explosion of even the fastest cordite was, by means of this instrument, accurately inscribed without any oscillations being set up in the mechanism of the recorder. The pressures measured range from 100 to 1800 atmospheres (0·7 to 12 tons per square inch).

Many of the results obtained during the study of cordite are most easily

* Living, 'Proc. Camb. Phil. Soc.,' vol. 12, p. 337.

expressed graphically, and a study of the curves given in the paper will be found preferable to the most careful abstract. In dealing with such a subject, general statements bereft of the necessary explanations and qualifications are apt to be somewhat misleading.

The present investigation confirms the view that the combustion of cordite proceeds according to parallel surfaces. The rate at which the flame travels towards the centre of each particle of explosive is proportional to the pressure under which combustion is taking place.

This velocity is measured and it is shown how both the time required to reach the maximum pressure, and also the shape of the curve representing the rise of pressure, may be calculated from the data given.

The effect produced by decreasing the diameter of the explosive is discussed. Though the time required for complete combustion decreases with the diameter, the shape of the curve representing the rise of pressure remains practically unaltered, the scale of time alone being changed. Thus, even were the cordite in the finest state of division, though the combustion would be nearly instantaneous the effect produced would always be distinct from that of a detonation.

The maximum pressures obtained are compared with the measurements made by Noble with which they are in close agreement. It is shown that the pressure developed by the explosion for various gravimetric densities may be deduced, with a fair degree of approximation, by formulæ derived from the kinetic theory of gases. The pressures calculated according to Van der Waals' law are compared with the experimental results.

The modifications introduced by the use of enclosures of different shapes are studied. When the surface of the enclosure is considerable as compared with its volume, the diameter of the cordite has a marked influence on the maximum pressure developed. For large diameters the pressure is considerably below the normal value.

With regard to the rate of cooling the results are compared with those obtained by the author in previous experiments on gases under high pressures.* The investigation leads to the conclusion that the rate of cooling depends essentially on the thermal conductivity of the enclosure and not on that of the gas.

With the massive enclosures which are necessary for such experiments, it is found that the rate of cooling varies, not in proportion to the surface but more nearly as the square of this value. Incidentally attention is drawn to the very high temperatures which are reached by the inner surface of the steel walls. This throws some light on the important question of erosion.

* 'Phil. Trans.,' A, vol. 197, pp. 229 to 254, 1901.

When the explosion takes place in a long vessel, wave action is frequently set up. A non-uniform distribution of the explosive enhances this phenomenon. The velocity of the pressure-wave is measured and compared with the velocity of sound under similar conditions. Generally speaking the work confirms the remarkable properties of cordite with regard to its high power and to the regularity of the effects produced.

The paper is accompanied by some 20 figures illustrating the results obtained, and is followed by tables giving the principal numerical values.

The Flow of the River Thames in Relation to British Pressure and Rainfall Changes.

By Sir NORMAN LOCKYER, K.C.B., LL.D., Sc.D., F.R.S., and WILLIAM J. S. LOCKYER, M.A. (Camb.), Ph.D. (Gött.), F.R.A.S.

(Received April 5,—Read May 18, 1905.)

[PLATES 6 AND 7.]

In a previous communication* to the Society we gave the results of a preliminary survey of the behaviour of the short-period barometric variation over many areas on the earth's surface. The very close association of rainfall with pressure has led to an enquiry into the variation of the former in relation to this latter change; this investigation is still in progress.

The recent publication, July 18, 1904, of a memorandum to the Thames Conservators on the "Rainfall and Floods in the Basin of the River Thames above Teddington Weir" since the year 1883, and a previous report on "The Shrinkage of the Thames and Lea," published by the London County Council in 1903, present data the discussion of which, although belonging to the general investigation to which reference has just been made, forms rather a subject for special enquiry and makes a reference to it desirable at the present time.

The present communication is, then, strictly limited to these and other data which have been collected in Britain. The relation to the questions of rainfall and pressure changes over large areas is, however, discussed. Reference to the Lea has here been omitted, since this river has been stated in the above-mentioned report of the L.C.C. to exhibit variations similar to those of the Thames.

* 'Roy. Soc. Proc.,' vol. 73, p. 457.

Among the flood statistics given in the memorandum are tables showing the total quantity of water flowing over Teddington Weir, with the addition of the water abstracted by the Water Companies. These tables are three in number, and give the flow for the whole year and for the summer (April and September) and winter (October to March) months from 1883 to 1903. Similar tables are also inserted showing the average rainfall, for the same period, at 12 stations in the basin of the River Thames above Teddington.

In the present discussion the year has been divided according to the mean annual variation curves of the phenomena dealt with. In the case of rainfall for the British Isles, the 12 months from April 1 to March 31 of the following year have been employed (*see* fig. 1). April being the month when the rainfall is at about a minimum, this month, together with the 11 months following, thus include a complete rainfall cycle.

In the curves for rainfall—and the same holds good for those of pressure—the mean yearly values are plotted in September of each year; thus the point inserted for the year 1884 represents the mean value for the period April 1, 1884, to March 31, 1885.

For the river data a different grouping of the months is employed. This was necessary since the flow followed the rain instead of being synchronous with it. This apparent “lag” of the river’s response to the rainfall is shown also in the accompanying figure (fig. 1), and it will be seen that the minimum or maximum flow values are *five months after* those of rainfall.

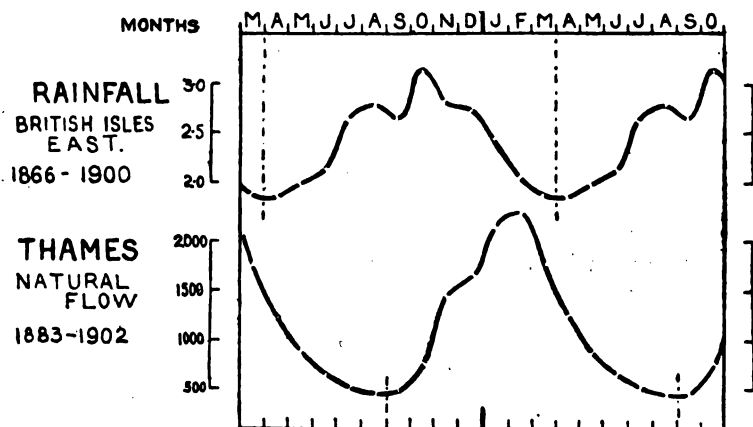


FIG. 1.—Curves to illustrate the relation between the mean annual Variation of Rainfall for the British Isles and the mean annual Variation of the Flow of the River Thames.

For the river data, then, the year has been taken to commence in the beginning of September and end on the last day of August of the following year. The centre of the period being the month of February, each yearly

value might have been plotted in this month, but it has been placed under that of the rainfall corresponding to this flow—*i.e.*, under September of the preceding year. Thus the rainfall from April, 1903, to March, 1904, which is the last point plotted on the curves in Plate 6, is placed vertically over the point representing the river flow as measured between September, 1903, and August, 1904. (See Plate 6, Curves III and IV.)

The accompanying table (Table I) gives the data published by the Thames Conservancy computed on the above scheme, and these values put in the form of curves in Plate 6 (Curves III and IV) and indicated by continuous lines.

Table I.—Natural Flow at Teddington Weir compared with the Average Rainfall of Twelve Stations in the Thames Valley.

Year.	Natural flow in millions of gallons. Sept.—Aug.	Actual rainfall in inches. Apr.—Mar.	Year.	Natural flow in millions of gallons. Sept.—Aug.	Actual rainfall in inches. Apr.—Mar.
1882-3 ...	(817,492)*		1893-4.....	328,938	22.7
1883-4 ...	459,085	26.5	1894-5.....	665,770	31.0
1884-5 ...	328,899	23.7	1895-6.....	329,922	26.0
1885-6 ...	563,333	28.1	1896-7.....	645,548	30.4
1886-7 ...	521,042	29.9	1897-8.....	277,159	22.0
1887-8 ...	371,635	22.2	1898-9.....	392,499	25.7
1888-9 ...	542,673	28.1	1899-1900	450,159	27.5
1889-90...	341,527	25.4	1900-1.....	334,685	24.3
1890-1 ...	226,771	21.7	1901-2.....	232,249	23.0
1891-2 ...	595,905	32.1	1902-3.....	520,766	27.0
1892-3 ...	450,247	26.3	1903-4.....	851,605	41.7
Total, 1883-1904.....			9,425,367		565.3
Average, 1883-1904.....			448,827		27.0

In order to deal with as long a period as possible, an attempt has been made to determine the flow for years previous to 1883. By the kindness of the Conservators of the River Thames, to whom application was made for any available data, permission was given to abstract valuable information existing in their archives. This afforded a means of obtaining a good general idea of the behaviour of the river from March 1, 1859.

This record is given in the form of daily readings in feet and inches of the level of the river at the Lower Sill at Teddington. Monthly means of these

* This value is obtained by adding the flow computed from the height of the river observed during September to December, 1882, to the actual flow measured during January to August, 1883. (See also Table II.)

values were then formed, and finally, annual means for the 12 months beginning in September and ending the following August; these annual means from 1860-1883 were then put in the form of a curve. This curve indicated a prominent short-period variation of about three years, and there was a general tendency of the curve as a whole to give readings of less height on the average year by year. Such a gradual change, since the zero of the sill remained constant, could only be due either to a long-period variation in the supply of water to the river at the sill or to the result of the lowering of the river bed by dredging or natural causes. The only information with regard to the latter that could be obtained was that, previous to 1879, dredging had been in progress, but to what extent was unknown.

It was, therefore, thought advisable to look upon this gradual apparent lowering of the water surface as due to dredging, and therefore eliminate it. The amount was, however, small, namely 8 inches in 23 years, and consequently had little effect on the resulting values of the sill readings. This was accomplished in the final step of converting the sill readings into flow. The method of reduction was to use the relationship between the depth of the lower sill (DLS) and the flow in millions of gallons per day which the Conservators had found to exist and had utilised since 1883.

The formula

$$(DLS - 5 \text{ feet } 3 \text{ inches})^2 40.35$$

represents the flow in millions of gallons per day, where DLS is the reading of the depth of the lower sill and the two other numbers constants for the year 1883.

In the reduction of the mean yearly values of the sill readings allowance was made for this apparent lowering of the water level between 1860 and 1883, and the resulting values of flow for each year are given in the third column of Table II; the second column shows the corresponding sill readings. The above values have been put in the form of a curve (Plate 6, Curve III, broken line portion).

In the above figures and curves no allowance has been made for the water abstracted by the Water Companies. This, however, does not materially affect the values as the quantity is relatively small. Further it would only make the curve for this period, 1860-1883, higher than it is at present.

Since 1883 the water abstracted by the companies has risen from 30 to 50 thousand millions of gallons per year, and as the mean value of flow in the same period is 412 thousand million gallons, this means that the withdrawal has risen from 7 to 12 per cent.

It is fair to assume, therefore, that less than 30 thousands of millions of gallons were extracted annually before 1883. If we take 20 thousands of

Table II.—Height and Computed Flow of the Thames at Teddington compared with the Average Rainfall of "England South."

Year.	Height in feet and inches. Sept.—Aug.	Computed flow in 1000 million gallons. Sept.—Aug.	Rainfall in inches. Apr.—Mar.	Year.	Height in feet and inches. Sept.—Aug.	Computed flow in 1000 million gallons. Sept.—Aug.	Rainfall in inches. Apr.—Mar.
	ft. in.				ft. in.		
1859-60	13 1	758		1871-2	12 3	658	32.7
1860-1	13 5	826		1872-3	13 1	835	40.0
1861-2	12 9	698		1873-4	11 5	511	22.5
1862-3	12 0	562		1874-5	12 2	658	28.9
1863-4	12 3	607		1875-6	12 10	802	34.1
1864-5	12 4	634		1876-7	12 9	790	36.9
1865-6	12 11	752		1877-8	11 8	580	29.5
1866-7	13 1*	797*	31.5	1878-9	12 11	836	32.4
1867-8	11 11	577	27.7	1879-80	11 6	562	28.7
1868-9	12 9	736	31.7	1880-1	12 4	730	34.5
1869-70	11 11	589	27.1	1881-2	11 4	542	25.5
1870-1	11 5	496	22.8	1882-3	(12 9)	(817†)	35.2
Total, 1867-1882.....					182 3	9902	455.0
Average, 1867-1882.....					12 2	660	30.3

millions of gallons as a possible mean annual value abstracted during the period 1867-1883, then, since the mean computed flow for this period amounts to 660 thousands of millions of gallons, only about 3 per cent. of the flow was utilised. Such a quantity becomes practically negligible and can, therefore, be left out of consideration.

Having thus secured a more or less homogeneous series of observations from the Teddington gauge, an attempt was made to check the curve thus obtained by the readings of another gauge in a different part of the river. With this intention inquiries made at the Thames Conservancy Offices, led us to communicate with Mr. Brough Taylor, who informed us that his late father, as Chief Engineer of the Lambeth Water Works, made a series of gaugings, commencing in 1860, of the Thames at Ditton. A request to the present engineer of the Metropolitan Water Board, Mr. Thomas F. Parkes, for information on this subject, resulted in the loan of books containing records of the daily heights of the river at Surbiton from June, 1863, to December, 1904.

* There being no record of the height during June, July, August, and September, in 1866, the means of the heights recorded during these four months in the four preceding and the four following years have been used.

† See note to Table I.

We take this opportunity of returning our thanks to those mentioned above for their willing assistance.

The treatment of these data was the same as that adopted for the Teddington gauge readings. The monthly means were first formed from the daily readings, and then the mean values of the months from September to August of the following year determined. In this way a series of mean annual values of the level of the river at Surbiton was obtained, but it was found impossible to convert this into flow, as the necessary data were not available; further, for the same reason, no allowance has been made for the water abstracted by the water companies. The following table contains the values thus employed:—

Height of the Thames in Relation to "Mean Summer Level" at Surbiton.

Year. Sept.—Aug.	Height in feet.	Year. Sept.—Aug.	Height in feet.	Year. Sept.—Aug.	Height in feet.
1863-4	+0.17	1877-8	+1.11	1891-2	+1.08
1864-5	+0.18	1878-9	+1.81	1892-3	+0.67
1865-6	+1.22	1879-80	+0.85	1893-4	+0.44
1866-7	+1.29	1880-1	+1.54	1894-5	+1.05
1867-8	+0.37	1881-2	+1.05	1895-6	+0.38
1868-9	+0.92	1882-3	+1.92	1896-7	+1.02
1869-70	+0.46	1883-4	+0.64	1897-8	+0.33
1870-1	-0.22	1884-5	+0.44	1898-9	+0.69
1871-2	+0.92	1885-6	+1.02	1899-1900	+0.83
1872-3	+1.68	1886-7	+1.13	1900-1	+0.50
1873-4	+0.50	1887-8	+0.75	1901-2	+0.33
1874-5	+1.14	1888-9	+0.90	1902-3	+0.83
1875-6	+1.57	1889-90	+0.46	1903-4	+1.49
1876-7	+1.90	1890-1	+0.24		
				Total	35.90
				Mean	0.875

In Plate 6 (Curve II) these values are given, and it will be seen that the variations from year to year corroborate in a striking manner those indicated by the curve of the river flow at Teddington.

These two curves may then be taken to represent the changes from year to year (September to the following August) that the Thames undergoes in consequence of the variation in the supply of water to the river. In the memorandum to the Thames Conservators, to which reference has already been made, the very intimate relation which must necessarily exist between the rainfall of the basin and the river's discharge, was clearly pointed out for the period 1883 to 1903 (*see* Plate 6, Continuous Curves III and IV).

The rainfall curve employed in the memorandum represents only a comparatively small area of the British Isles, and only commenced in the year 1883.

It happens, however, that these rainfall variations in the Thames valley are not restricted to this small region, but are found to be similar to those which occur over a very large area in the British Isles. To illustrate this, use may be made of the very complete rainfall data for the British Isles, collected and reduced at the Meteorological Office and published in their annual summaries. The United Kingdom is divided into 11 districts for meteorological purposes, and according to this arrangement the Thames basin would be included in those termed England South* and Midland Counties.

Curves for these two regions are given in Plate 6 (Curves V and VI), and a reference to them will show that they represent changes which are very similar and correspond in time with those given for the Thames basin. If many other districts be compared in the same way, a similar type of variation is apparent. Thus Plate 6, Curve VII, illustrates the rainfall variation for the combined districts of Scotland East, England East and North-East, the Midland Counties, and England South.

In fact, it may be said that the Thames basin rainfall is that of the whole of the South, Midland, East and North-East of England and Scotland East. The other districts in the British Isles (with the exception of Scotland North, which is different to all other districts in the British Isles) are of a type similar to each other, but present variations which, although not widely different from the Eastern and other districts, are sufficiently unlike them to be classified apart.

Since all the above series of rainfall statistics commence in the year 1866, we have a means of comparing the rainfall with the Thames flow for a much longer period than was attempted in the Memorandum previously mentioned. Making such a comparison by means of the curves in Plate 6 (Curves II to VII), not only do the variations in both curves indicate the close relationship between the rainfall over this extensive region and the flow or height of the River Thames, but the flow variation curve is thus shown to be of considerable accuracy.

It may, however, be pointed out that it does not seem necessary to collect and discuss the data over *the whole* of this region before any deduction for practical purposes can be made as to the flow of the Thames. The rainfall and barometric observations made at the Oxford Observatory (Radcliffe) exhibit variations from the year 1860 up to the present time so very similar to those of the Thames flow that the curves are very nearly interchangeable. So striking is the agreement that curves illustrating these

* *England, South*, comprises the counties of Dorset, Hampshire, Kent, Middlesex, Surrey, and Sussex. *Midland Counties* include Gloucester, Hereford, Leicester, Montgomery, Northampton, Nottingham, Oxford, Warwick, and York.

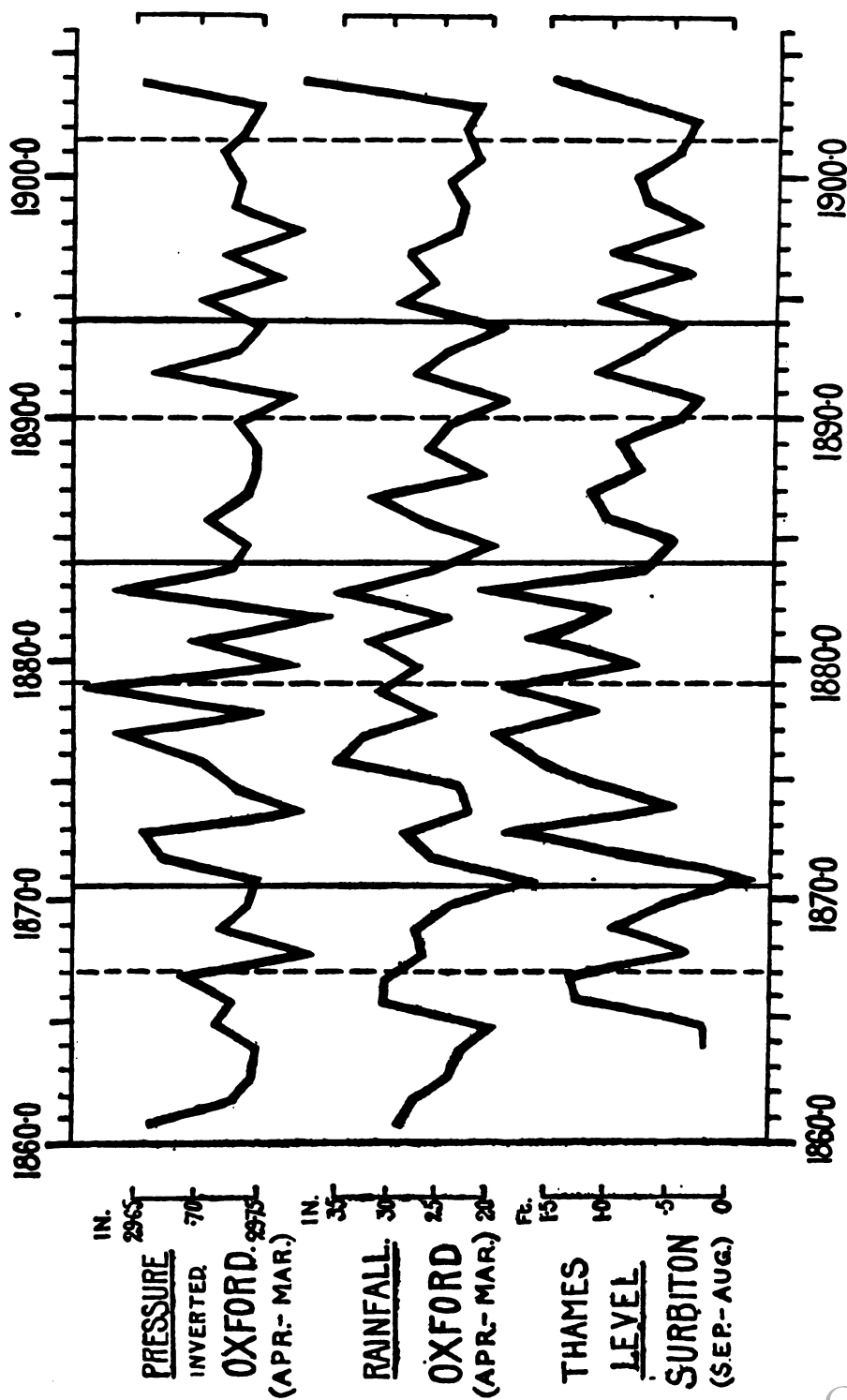


FIG. 2.—Oxford Rainfall and Pressure Changes in relation to Thames Level at Surbiton. (Vertical lines as in Plate 6.)

variations have been added in a separate diagram (fig. 2). In this the pressure and rainfall values are the means for the 12 months April to March, and the Thames level values the means for the year September to August.

The rainfall of the British Isles is produced mainly by the passage of areas of low barometric pressure travelling over the country in a north-easterly or easterly direction. It should be expected therefore that on the average the greater the rainfall the more numerous the cyclones, and consequently the lower the mean value of pressure. For the greater part of the United Kingdom, therefore, the rainfall variation from year to year should correspond very closely with the inverted pressure change. That this condition is actually fulfilled can be judged by comparing in Plate 6, Curve VIII, representing the barometric variation (curve inverted) from year to year at Oxford with the rainfall curves given below it. Instead of Oxford, any other town in the United Kingdom such as Armagh, might have been given, for the pressure changes from year to year are remarkably similar over a very extensive area. So far then it has been shown that with reference to this short-period variation the pressure, rainfall, and river flow are all intimately related, and any method of forecasting the pressure changes would make it possible to determine beforehand the rainfall.

Since the Thames flow values have a lag of about five months on both rainfall and pressure, a means is possibly available of stating the expectancy of excessive or deficient amount of water in the river.

In addition, however, to this short-period variation, there is an apparent longer change indicated in all the curves. To render the latter more clear three-year means have been formed for each of the curves and the curves re-plotted in Plate 7.

An examination of these curves shows that in those years when the river flow was greatest, *i.e.*, between about the years 1873–1883, the rainfall was highest, and the mean pressure lowest, which is exactly what was to be expected from the relationship between pressure, rainfall, and river-flow in these Islands. The main points, however, which these curves clearly indicate are that this long-period change in each of them is real, and that the low river levels, deficiency of rainfall, and excess pressure of the last series of years are now about to be followed by greater mean flow of the River Thames, increase in the mean rainfall and deficiency of the mean pressure.

In a previous communication, to which reference has already been made, we pointed out with regard to the behaviour of the short-period pressure variations taking place over the Earth's surface that:—*

* In some regions the pressure variation curves were distinctly a mixture

* 'Roy. Soc. Proc.,' vol. 73, p. 458.

of both Indian and Cordoba types, and it was difficult to classify them satisfactorily"

One of these regions of mixed-type pressures included Western Europe, comprising the British Isles, Holland, Belgium, France, Spain, Germany, Italy, etc. To illustrate the nature of this British variation in relation to the two main types represented by India and Cordoba (which are the inverse of each other) fig. 3 is added. These curves show the changes of the mean annual values of pressure from year to year, the year being reckoned here from January to December. The uppermost curve represents an hypothetical curve with a period of 3·8 years, and beneath it is given the Cordoba pressure curve. The hypothetical curve was made to fit that of Cordoba as near as possible, and it will be seen that there is very close agreement on the average, with the exception of the years 1892 and 1900 to 1903. At the bottom of the plate is given the *inverse* of the hypothetical curve shown above and the Indian pressure variation curve.*

These two latter curves, also from the year 1873, are in the main very similar, with the exception of the years 1892 and 1901–1903. Previous to 1873 the observed maxima and minima anticipate those of the hypothetical curve.

Between the Cordoba and Bombay curves is placed that of Oxford, representing the barometric changes occurring over the British Isles.

A comparison of these three curves indicates the intermediate nature of the Oxford variation in relation to those of Cordoba and India. The following table gives a statement of the years in which either excessive high or low pressures at Oxford were coincident with corresponding excesses in India or Cordoba :—

Agreement of Oxford with—	Years of simultaneous excess.	
	High pressure.	Low pressure.
Cordoba	1874	—
"	1875	—
"	—	1877
India	—	1878
"	1880	—
"	—	1882
"	1884	—
"	—	1886
Cordoba	1893	—
"	—	1895
India	1896	—
"	1899	—

* It will be noticed that the points of maxima of the hypothetical curve at the top of the plate do not lie midway between the minima on either side of them, but nearer the

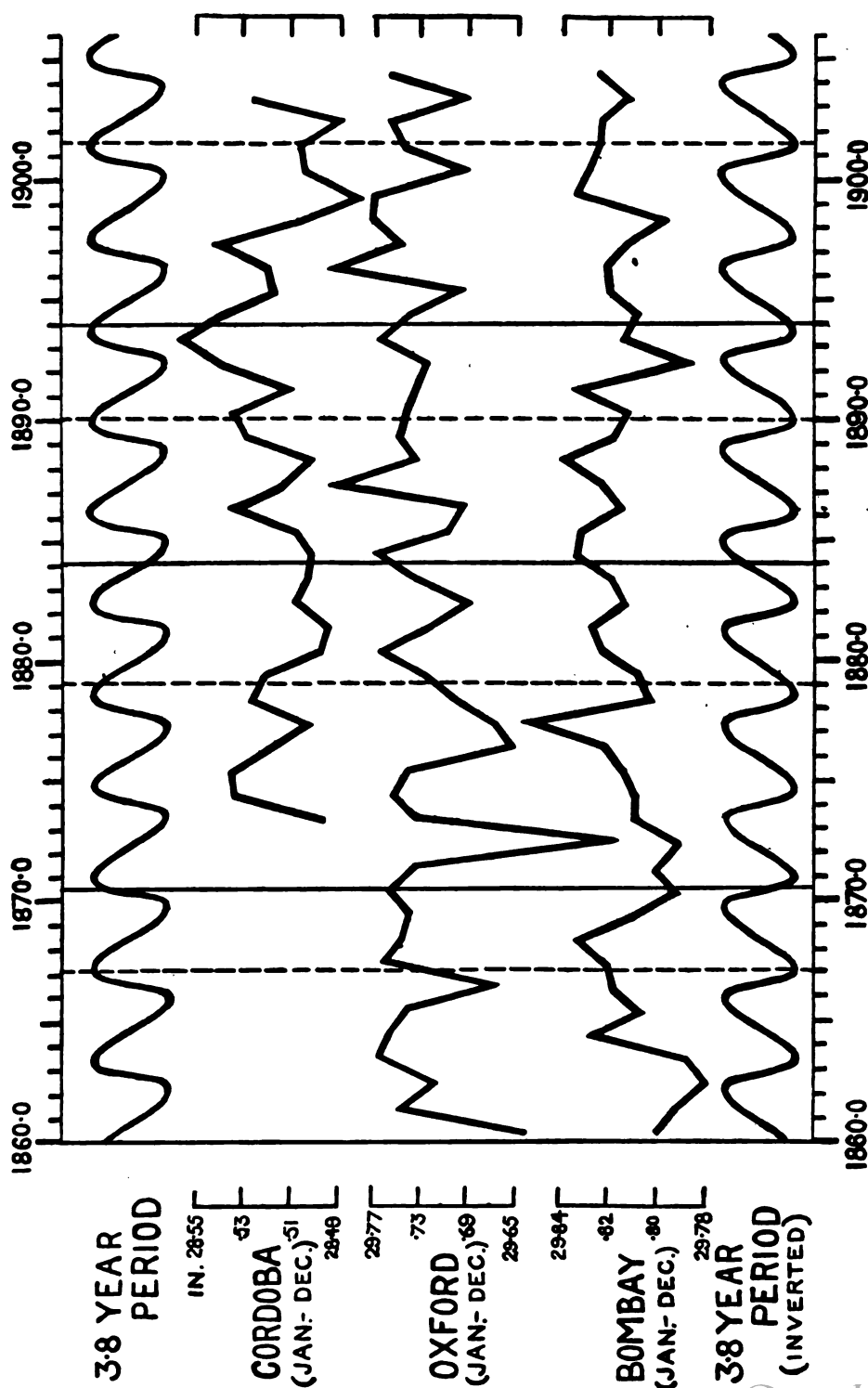


FIG. 3.—British Pressure Change in relation to Indian and S. American Pressure Variations. (Vertical lines as in Plate 6.)

From this it will be seen that there seems to be a very even balancing between Cordoba and India, the former claiming coincidences with Oxford of three excess highs and two lows, while the latter has four excess highs and three lows.

An interesting point which the above table clearly brings out is that the Oxford curve seems to favour for series of years the two main pressure types *alternately*. Thus, from 1874 to 1877 the curve more resembles Cordoba, from 1878 to 1887, India; from 1888 to 1895, Cordoba again, and from 1896 to 1899, India.

From 1900, as far as observations are available, the type of variation is indefinite.

It is possible that it is this alternate reversion from one type to the other that prevents the 3·8 year change of the Indian and Cordoba curves from occurring in the British curves, and substitutes for it an apparent shorter period of about three years, which is very noticeable in all the British curves shown in Plate 6.*

A closer study then of the British pressure changes in relation to those of the Indian and Cordoba regions may, therefore, throw considerable light on the pressure changes occurring in these islands.

With regard to the long-period changes which are taking place in the British Isles, the subject will not be referred to here at any great length as it is still under discussion. There is, however, sufficient evidence to show that this British variation is different in length of period from that in action in the Indian region, while the latter is again different from the long-period changes occurring in the Cordoba region. This inquiry is one of great interest, but lack of sufficient data has delayed the completion of the investigation. It is hoped, however, soon to communicate the results when these requirements have been fulfilled.

The curves in Plate 7 give a general idea of the long-period British variation that is in progress, and there seems evidence that the minimum of this change has already passed. As the length of this period is about 35 years, and the last maximum occurred in the years about 1878, the curves should now all rise until about the year 1913, when the next maximum may be expected. On the average, therefore, during the next decade preceding minimum. The curve was drawn in this manner because it was found that, when a symmetrical curve was inverted, it did not correspond well with the Indian pressure curve, while an unsymmetrical one, as shown, made a better agreement.

* Previous to the year 1879 this hypothetical three-year curve begins to disagree with the actual observed values, the maxima and minima of the latter anticipating those of the hypothetical curve. A similar kind of disagreement was also noticed in the curve of Indian pressure changes (previous to 1873) and the 3·8 hypothetical curve.

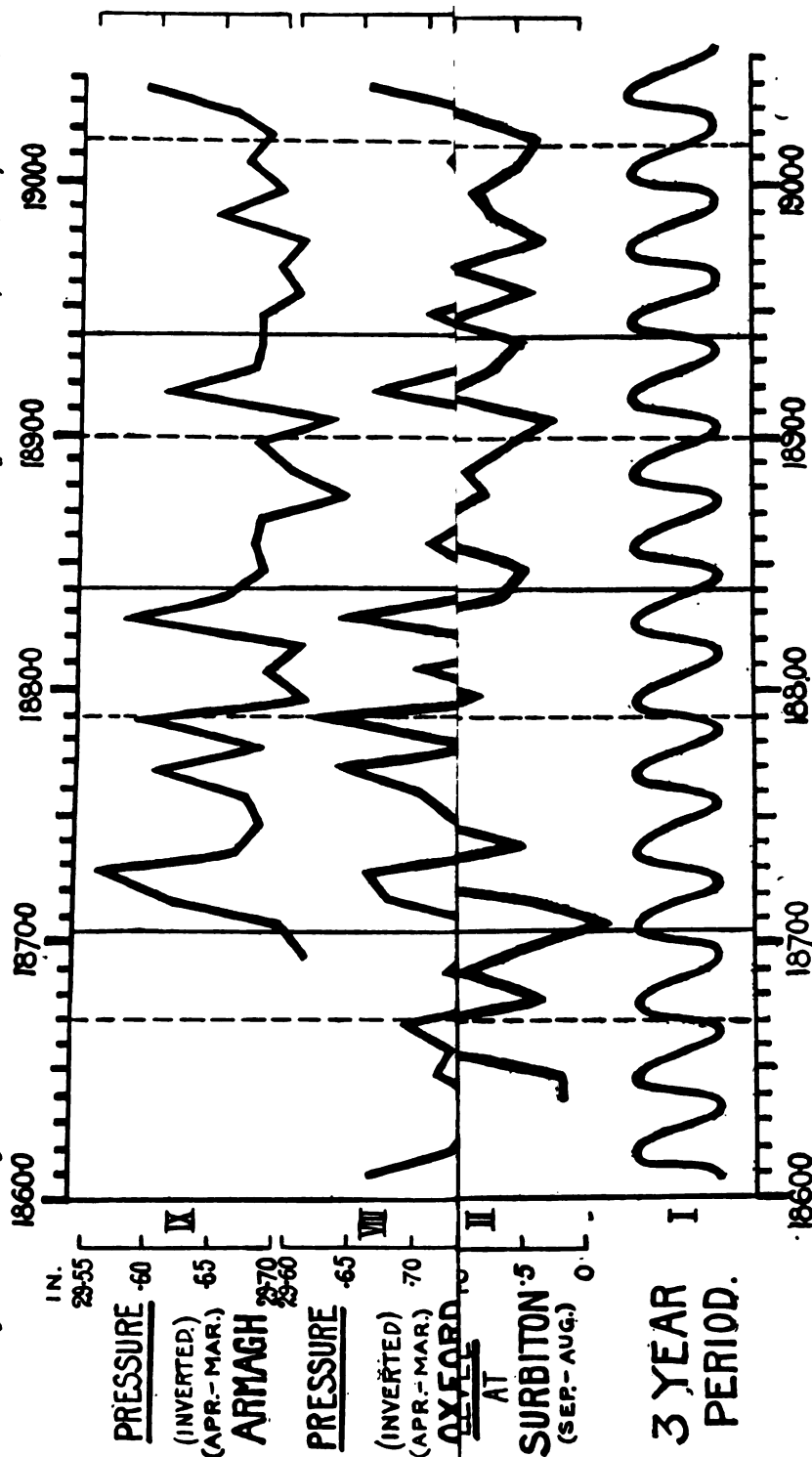
pressure should decrease, rainfall should increase, and the Thames flow become greater.

In addition to those to whom reference has already been made, we wish to express our thanks to Messrs. W. Moss and T. F. Connolly for assistance in the computations and drawing of the curves.

Conclusions.

The above discussion indicates that the following deductions may be made :—

1. The Thames flow has a lag of about five months on the rainfall occurring in the Thames Basin.
 2. The flow is closely associated with the rainfall of this basin.
 3. The rainfall variations of the Thames Basin are identical with those of the larger portion of Great Britain, more particularly the eastern regions.
 4. These rainfall changes vary inversely with the pressure changes that occur over the whole of the British Isles.
 5. The British pressure variation is closely associated with the barometric see-saw occurring between the Indian and South American regions.
 6. For all practical purposes the pressure and rainfall data of one station, namely, the Radcliffe Observatory, Oxford, are sufficient to indicate very closely the subsequent changes in the Thames flow.
-



Curves to illustrate the Similarity between the Short-period Changes of Pressure (curves inverted), Rainfall, and Thames Flow, in the British Isles. (The continuous and broken vertical lines represent the epochs of sunspot maxima and minima, as determined from the mean daily areas of both hemispheres of the sun.)

*Preliminary Report on a Survey of Magnetic Declination near
the Royal Alfred Observatory, Mauritius.*

By THOMAS FOLKES CLAXTON, Director.

(Communicated by Dr. C. Chree, F.R.S. Received June 22, 1905.)

The accompanying chart is a graphic representation of the results of a survey of magnetic declination over a portion of the grounds of the Royal Alfred Observatory, Mauritius, which originated as follows:—

Absolute determinations of the magnetic elements have been made with instruments of the Kew pattern since the year 1875, and in the year 1903 it was decided to utilise the 12-inch theodolite for more refined observations of declination. For this purpose its vertical pillar was removed and a brass one substituted. Suitable experiments showed that the small steel screws in various parts of the instrument had no sensible effect on the declination magnet when at a distance of 4 feet from the theodolite.

It was considered advisable to mount the new apparatus as near as possible to the old magnetic pavilion, but at a sufficient distance to avoid sensible interaction of the magnets during the observations of dip and horizontal force in the old pavilion.

It was further desirable that the spot selected should command a view of the astronomical mark on Pieter Both, a hill some six miles to the south. The mark formerly used is only 150 yards to the south of the old pavilion. A concrete pillar for the theodolite was accordingly erected 90 feet to the south (magnetic) of the old declinometer pillar, and a pavilion built over it 12 feet long by 7 feet wide and 10 feet high. The magnet was mounted on a solid teak table 6 feet to the south of the theodolite, and it was found that at this spot the declination was $10^{\circ} 35'$ (west), or $1^{\circ} 20'$ greater than on the old declinometer pillar 90 feet to northward.

Observations at intermediate points gave the results shown on p. 508.

On November 4 observations were taken along a line running east-south-east from Station No. 4, at intervals of from 10 to 30 feet, and on November 7 at intervals of 10 feet in a direction south-south-east from the same station.

When plotted on a chart, however, the results showed that observations at much closer intervals were necessary before accurate isogonic lines could be drawn; the instrument was therefore made to slide along a plank, to the sides of which wooden runners were attached, serving as guides for a grooved support carrying the instrument. Holes were drilled in the plank at

Date, 1904.	Number of station.	Rectangular co-ordinates from old declinometer pillar.		Observed value of declination (west).	Magnetograph reading.	Comparative values of declination.
		South (astronomical).	East (astronomical).			
d. h. m.		feet.	feet.	° ' "	' "	° ' "
October 24 9 5...	1	+72.7	+9.6	10 1	9	9 52
9 27...	2	+51.4	+6.6	9 30	9	9 21
9 53...	3	+38.9	+5.3	9 19	9	9 10
10 20...	4	+15.8	+3.0	8 24	9	8 15
10 37...	5	+20.0	+3.6	8 16	8	8 8
11 5...	6	+23.1	+3.8	8 19	8	8 11
11 32...	7	+26.4	+3.9	8 32	7	8 25
11 50...	8	+30.0	+4.0	8 43	6	8 37
12 15...	9	+34.4	+4.4	8 59	5	8 54
12 39...	10	+21.8	+3.7	8 14	4	8 10

intervals of 6 inches, and after setting up the plank on trestles, in any desired position, the declinometer was accurately centred over the first hole and its position determined, with plumb line and tape, by triangulation from certain fixed points. After observing over each hole in succession the position of the declinometer was again determined when centred over the last hole, and intermediate positions obtained by interpolation.

Care was taken to keep the magnet as nearly as possible at a constant distance (about 4 feet) from the ground throughout the survey; but the observations tend to show that perfect success in this respect was not obtained, and two or three sets near one of the foci were rejected, as the plotted results indicated that the plank was either too high or too low. Observations at one station gave $12^{\circ} 40'$ (west) as the declination at 4 feet from the ground, and $14^{\circ} 0'$ (west) at 2 feet above the ground.

Plotting the position of the plank on a chart, together with the results of the observations as soon as completed, showed where other observations were necessary, and in this manner the various foci were located without unduly multiplying the observations, the intervals being suited to the declination gradient. At some places it was necessary to observe at the beginning and end of the plank only, while at the first focus discovered the declination was changing so rapidly that the plank was discarded and observations taken at rectangular intervals of 3 inches, on a table ruled and grooved for this purpose.

Thus the survey became extended until sufficient (893) observations were obtained to construct the accompanying chart.

The labour of observation and reduction was lightened by using a subsidiary theodolite, placed in view of the astronomical mark and at a

sufficient distance from the declinometer. The reading on the horizontal circle of the theodolite corresponding to the astronomical meridian was obtained by measuring the distance of the theodolite east or west of the transit instrument, and from observation of the mark, which bears due south from the transit instrument. It was then only necessary to observe the bearing of the middle of the declinometer with the theodolite, and *vice versa*, to obtain the reading on the declinometer corresponding to the astronomical meridian.

Three well marked foci were detected, as follows :—

Focus.	Phase.	Rectangular co-ordinates from old pillar.		Declination reduced to a constant magneto- graph reading.	Distance between maximum and minimum.	Mean gradient from maximum to minimum.
		South.	East.			
1	Maximum	feet. +16·3	feet. +24·7	° ' 10 45	feet. 11·4	1° in
	Minimum	+18·3	+13·5	4 56		1·9 feet
2	Maximum	+51·4	—13·7	13 45	8·5	1·1 "
	Minimum	+53·4	—22·0	6 20		
3	Maximum	+34·3	+95·6	12 50	23·5	4·6 "
	Minimum	+38·0	+72·6	7 45		

Notwithstanding the 893 observations from which the accompanying chart has been constructed, the true undisturbed value of the declination at the observatory is by no means evident. About midway between the old and new piers the isogonic line of $9^{\circ} 30'$ forms a triangle, of about 200 square feet area, towards the centre of which the declination decreases to $9^{\circ} 20'$. From the north-west angle of the triangle the declination increases rapidly towards the west, on the south side increases towards the south, and on the east side decreases towards the north-east and increases towards the south-east.

Were this the only "plateau" shown on the map a value between $9^{\circ} 20'$ and $9^{\circ} 30'$ might be assumed as the true declination; but between 30 and 50 feet to the east-north-east of the old pier the isogonic line of 10° forms an ellipse, of about 500 square feet area, over which the declination is nearly constant, except to the north-west of its centre where the declination increases to $10^{\circ} 10'$. Another area of relatively shallow gradients is that immediately to the north-west of the old pier, particularly between the isogonic lines of $9^{\circ} 30'$ and $9^{\circ} 45'$.

It appears, therefore, that the normal declination at the Royal Alfred Observatory, Mauritius, is about $9^{\circ} 45'$, or $30'$ greater than the value

510 Mr. T. F. Claxton. *Magnetic Declination near* [June 22,
obtained on the old pier, used for the values published in the annual volume
of meteorological and magnetical observations since the year 1875.

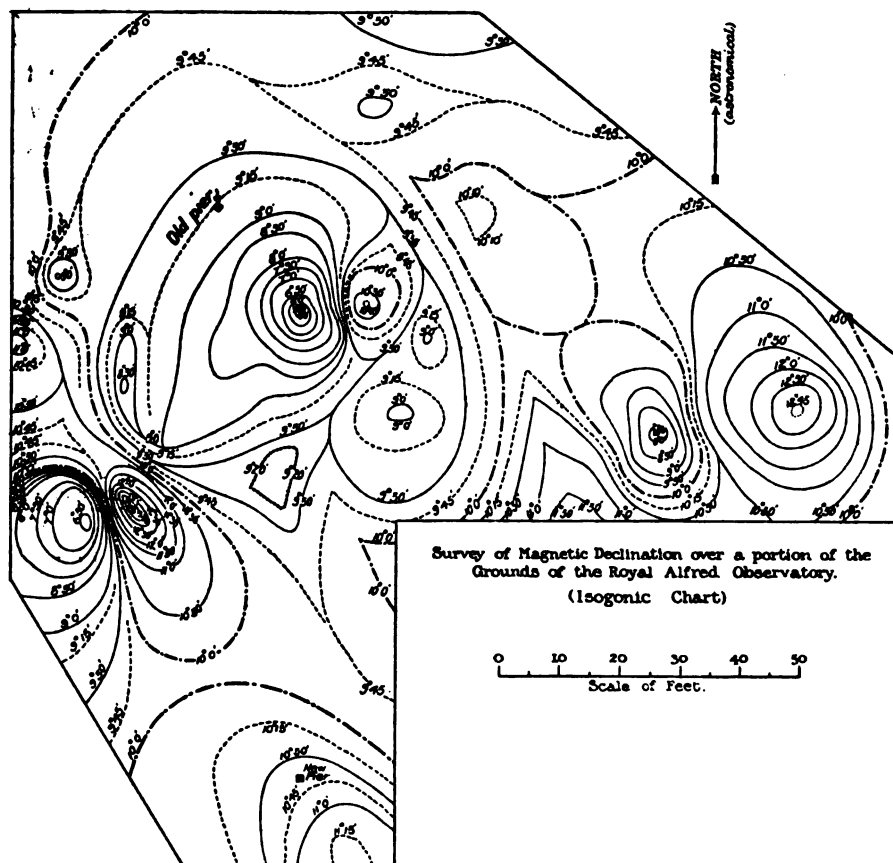


FIG. 1.

In the year 1899 observations of magnetic declination were made at 23 stations in different parts of the island; the two extreme values, $11^{\circ} 29'$ (west) and $7^{\circ} 30'$ (west), were obtained at points separated by only 400 yards, while the mean of the 23 values was $9^{\circ} 25'$. The horizontal force was observed at twelve, and the dip at six of these stations. The mean results were for horizontal force 0.2310 (C.G.S. unit) and for dip $55^{\circ} 4'$ (south).

The horizontal force and dip were observed near the two principal foci detected at the observatory, with the following results:—

Focus.	Station.	Rectangular co-ordinates from old pillar.		Observed.		Resulting.	
		South.	East.	Horizontal force.	Dip (south).	Vertical force.	Total force.
1		feet.	feet.	(C.G.S.).	° ' "		
	A	+ 18.1	+ 19.2	0.2282	53 26	0.3077	0.3831
	B	+ 16.7	+ 19.4	0.2355	52 16	0.3043	0.3848
	C	+ 21.7	+ 19.9	0.2439	51 56	0.3114	0.3955
2	D	+ 54.6	- 16.6	0.2400	50 28	0.2908	0.3770
	E	+ 47.7	- 19.6	0.2011	55 37	0.2939	0.3561
	F	+ 46.7	- 20.5	0.1989	57 36	0.3103	0.3875
	G	+ 46.0	- 21.3	0.1993	58 34	0.3261	0.3813
	H	+ 58.6	- 15.2	—	50 47		
	I	+ 58.4	- 16.8	—	50 21		

Station B lies about midway between the positions of maximum and minimum (declination) of Focus No. 1. Stations E to I lie nearly at right angles to a line joining the positions of maximum and minimum (declination) of Focus No. 2.

It will be seen that from D to G, a distance of 9.7 feet, the dip varies $8^{\circ} 6'$, the horizontal force 0.0407 (C.G.S. unit), the vertical force 0.0353 (C.G.S. unit), and the total force 0.0043 (C.G.S. unit).

Researches on Explosives. Part III.—Supplementary Note.

By Sir ANDREW NOBLE, Bart., K.C.B., F.R.S., F.R.A.S.

(Received September 28, 1905.)

Since communicating to the Royal Society my Researches on Explosives, Part III, I have succeeded in obtaining the paper* by Messrs. Holborn and Austin on the Specific Heat of Gases at High Temperatures.

Their attention has been specially directed to carbonic anhydride, and their researches show a considerable (but rapidly decreasing) increment in the specific heat of CO_2 with increase of temperature.

If we suppose the same law of increment which appears to rule up to 800°C. to remain unaltered up to 1300°C. , the increments at that temperature would appear to vanish, and if this be so I find that the specific heat of CO_2 , at constant volume, should be taken at 0.2111.

I have therefore recalculated the specific heats given in my recent researches, the specific heats, at constant volume, which I have used being as follow:—

CO_2 .	CO.	H.	CH_4 .	N.	$\text{H}_2\text{O.}$
0.2111	0.176	2.411	0.470	0.175	0.368

and the recalculated specific heats of the exploded gases at the various densities come out as given below:—

For Cordite.

D = 0.50. 0.24454	D = 0.40. 0.24614	D = 0.30. 0.24691	D = 0.25. 0.24649	D = 0.20. 0.24556	D = 0.15. 0.24611
		D = 0.10. 0.24484	D = 0.05. 0.24515		

For M.D.

D = 0.45. 0.24498	D = 0.40. 0.24722	D = 0.30. 0.24795	D = 0.25. 0.24807	D = 0.20. 0.24908	D = 0.15. 0.25205
		D = 0.10. 0.24841	D = 0.05. 0.24882		

For Nitrocellulose.

D = 0.45. 0.24737	D = 0.40. 0.24716	D = 0.30. 0.24843	D = 0.25. 0.24766	D = 0.22. 0.25068	D = 0.20. 0.25065
		D = 0.15. 0.25210	D = 0.10. 0.25164	D = 0.05. 0.24963	

* 'Preuss. Akad. Wiss. Berlin Sitz. Ber.,' vol. 5, p. 175.

and these figures are, I think, to be preferred to those given in the tables where the specific heats used were those which had been determined for temperatures under 200° C.

The temperatures of explosion I am about to give have been obtained by two different methods—firstly, by dividing the heats determined by the calorimeter by the specific heats just given, and, secondly, using the equation of dilatibility of gases, and determining the temperature from

$$t = \frac{p - p_0}{0.00367 p_0}, \quad (1)$$

where p is the pressure in atmospheres obtained from the explosion, and p_0 the pressure in atmospheres when the volume of gases generated is reduced to 0° C. and 760 mm. Bar. Pressure.

The differences of the results are very remarkable.

Taking for example cordite as an illustration, it will be seen that for the four highest densities given the temperatures derived from the two methods are but slightly different. At the higher density (0.5) the temperatures are 5275° C. and 5263° C., the higher being that derived from Equation (1); at density 0.45 the temperatures from the two methods are identical, at density 0.40 the temperatures are 4902° C. and 4970° C., the lower temperature being from Equation (1), but after density 0.35 the temperatures derived from Equation (1) fall very rapidly.

The same general results are observable in the other two explosives experimented with, and it should be noted that in all three explosives, at the highest densities, the temperatures given by Equation (1) are greater than those obtained by the second method.

On the other hand the temperatures obtained by dividing the heat obtained from the calorimeter by the specific heat do not greatly differ, and the least difference rests with the cordite.

The figures for the three explosives are given below, the temperatures obtained from $\frac{\text{units of heat}^*}{\text{specific heats}}$ being given in italics.

Cordite.

D = 0.50.	D = 0.45.	D = 0.40.	D = 0.35.	D = 0.30.	D = 0.25.
5275°	5090°	4902°	4710°	4480°	4185°
<i>5263</i>	<i>5090</i>	<i>4970</i>	<i>4860</i>	<i>4800</i>	<i>4770</i>
D = 0.20.	D = 0.15.	D = 0.10.	D = 0.05.		
3838°	3490°	3140°	2775°		
<i>4760</i>	<i>4760</i>	<i>4790</i>	<i>4800</i>		

* Water gaseous.

M.D.

D = 0·45.	D = 0·40.	D = 0·35.	D = 0·30.	D = 0·25.	D = 0·20.
4718°	4494°	4200°	3920°	3585°	3240°
4624	4411	4215	4070	3945	3870
	D = 0·15.	D = 0·10.	D = 0·05.		
	2890°	2580°	2180°		
	3840	3330	3360		

Nitrocellulose.

D = 0·45.	D = 0·40.	D = 0·35.	D = 0·30.	D = 0·25.	D = 0·20.
4305°	4007°	3630°	3320°	3060°	2835°
3954	3890	3795	3670	3530	3425
	D = 0·15.	D = 0·10.	D = 0·05.		
	2680°	2520°	2400°		
	3345	3295	3255		

If these figures be examined it will be noted that in each explosive at the higher densities, the temperatures obtained by the two methods are nearly identical, those determined from Equation (1) being the higher, but as the density of charge is decreased the difference at the very low densities is remarkable; some of this difference is doubtless attributable to the slow burning under feeble pressures, and to the rapid cooling, by communication of heat to the walls of the explosive vessel during the ignition of the charge, but it is impossible to ascribe the whole difference to this cause, and I can only suggest that the explanation is to be sought in the probable dissociation of the carbonic anhydride and aqueous vapour at low pressures, this dissociation being prevented wholly or partially by the very high pressures at the higher densities.

Various substances such as carbon, metallic platinum, tantalum, osmium and titanium have been placed in the charge, and all have been more or less fused and volatilised during the small fraction of a second to which they were exposed to the maximum heat. Tantalum wire coiled on a steel wire became alloyed with the fused steel, taking up 14 per cent. Fe uniformly distributed, the Ta before the experiment being free from Fe.

A great part of the titanium was recovered in a fused crystalline condition.

Osmium and thin platinum foil were volatilised and thick sheet platinum was recovered in the form of a button.

On Newton's Rings formed by Metallic Reflection.

By RICHARD C. MACLAURIN, M.A., LL.D., late Fellow of St. John's College
Cambridge, Professor of Mathematics, Wellington, New Zealand.

(Communicated by Professor J. Larmor, Sec.R.S. Received August 15,—
Read November 16, 1905.)

In 1876, Sir G. Stokes brought to the notice of the British Association* a phenomenon of metallic reflection which he regarded as very remarkable. "When Newton's rings," he said, "are formed between a lens and a plate of metal, and are viewed by light polarised perpendicularly to the plane of incidence, we know that, as the angle of incidence is increased, the rings which are at first dark-centred, disappear on passing the polarising angle of the glass, and then reappear white-centred, in which state they remain up to a gauging incidence, when they can no longer be followed. At a high incidence the first dark ring is much the most conspicuous of the series.

"To follow the rings beyond the limit of total internal reflection, we must employ a prism. When the rings formed between glass and glass are viewed in this way, we know that as the angle of incidence is increased the rings one by one open out, uniting with bands of the same respective orders which are seen beneath the limit of total internal reflection; the limit or boundary between total and partial reflection passes down beneath the point of contact, and the central spot is left isolated in a bright field.

"Now when the rings are formed between a prism with a slightly convex base and a plate of silver, and the angle of incidence is increased so as to pass the critical angle, if common light be used, in lieu of a simple spot we have a ring, which becomes more conspicuous at a certain angle of incidence well beyond the critical angle, after which it rapidly contracts and passes into a spot.

"As thus viewed the ring is, however, somewhat confused. To study the phenomenon in its purity we must employ polarised light, or, what is more convenient, analyse the reflected light by means of a Nicol's prism.

"When viewed by light polarised in the plane of incidence, the rings show nothing remarkable. They are naturally weaker than with glass, as the

* 'Brit. Assoc. Report,' Glasgow, 1876; 'Math. and Phys. Papers,' vol. 5, pp. 361—364. Professor Stokes was at that time inclined to see in the phenomena the influence of a layer of gradual transition or whatever cause produced similar effects with diamond. The author learns from Prof. Larmor that Sir George Stokes had an intention for some time of examining theoretically the formation of Newton's rings on a metallic surface.

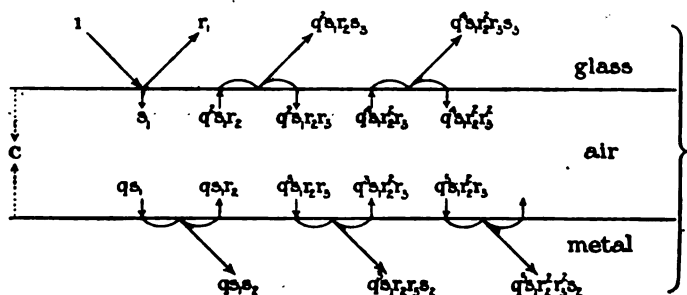
[The author is indebted to Dr. T. H. Havelock for the correction of the press.]

interfering streams are so unequal in intensity. They are black-centred throughout, and, as with glass, they open out one after another on approaching the limit of total reflection and disappear, leaving the central spot isolated in the bright field beyond the limit. The spot appears to be notably smaller than with glass under like conditions.

"With light polarised perpendicularly to the plane of incidence, the rings pass from dark-centred to bright-centred on passing the polarising angle of the glass, and open out as they approach the limit of total reflection. The last dark ring to disappear is not, however, the first but the second. The first, corresponding in order to the first bright ring within the polarising angle of the glass, remains isolated in the bright field, enclosing a relatively, though not absolutely bright spot. At the centre of the spot the glass and metal are in optical contact, and the reflection takes place accordingly, and is not total. The dark ring, too, is not absolutely black. As the angle of internal incidence increases by a few degrees, the dark ring undergoes a rapid and remarkable change. Its intensity increases till (in the case of silver) the ring becomes sensibly black, then it rapidly contracts, squeezing out, as it were, the bright central spot and forming itself a dark spot, larger than with glass, isolated in the bright field. When at its best it is distinctly seen to be fringed with colour, blue outside, red inside (especially the former). This rapid alteration taking place well beyond the critical angle is very remarkable. Clearly there is a rapid change in the reflective properties of the metal, which takes place, so to speak, in passing through a certain angle determined by a sine greater than unity.

"I have described the phenomenon with silver, which shows it best; but speculum-metal, gold, and copper show it very well, while with steel it is far less conspicuous."

It is with the object of accounting for these phenomena that the following investigation of Newton's rings formed by metallic reflection has been undertaken.



Suppose that we have a piece of glass and metal separated by a thin layer

of air of thickness c . A wave of unit amplitude represented by $e^{i(lx+my+nz-pt)}$ will at the passage from glass to air, give rise to a reflected wave $r_1 e^{i(lx+my+nz-pt)}$ in the glass and a refracted wave $s_1 e^{i(lx+my+nz-pt)}$ in the air. Let the quantities corresponding to r_1 and s_1 be r_2 and s_2 at the passage from air to metal, and r_3 and s_3 at the passage from air to glass. Suppose, further, that a wave of unit amplitude, represented by $e^{i(lx+my+nz-pt)}$, becomes $qe^{i(lx+my+nz-pt)}$ after traversing a distance c in air. Waves will be reflected to and fro between the glass and metal, and the waves that return into the glass will constitute a reflected beam represented by

$$r_1 + q^2 s_1 r_2 s_3 \{1 + q^2 r_2 r_3 + q^4 r_2^2 r_3^2 + \dots \text{ad inf.}\} \\ = r_1 + \frac{q^2 s_1 r_2 s_3}{1 - q^2 r_2 r_3}, \text{ provided } |q^2 r_2 r_3| < 1.$$

The values of the quantities r_1, r_2 , etc., will be given by the theory of reflection and refraction, and in this way we can easily prove that $r_1 + r_3 = 0$ and $s_1 s_3 = 1 - r_1^2 = 1 - r_3^2$, results that can also be obtained by means of Stokes' principle of reversion or by noting that when the metal is replaced by glass (so that r_2 and s_2 coincide with r_3 and s_3) and the thickness of the layer of air is indefinitely diminished and q becomes unity, then all the light is transmitted and none reflected. Making use of these relations we obtain for the reflected beam

$$r_1 + \frac{q^2 r_2 (1 - r_1^2)}{1 + q^2 r_1 r_2} = \frac{r_1 + q^2 r_2}{1 + q^2 r_1 r_2}.$$

In general r_1, r_2 , and q^2 will be complex quantities. We shall put $r_1 = R_1 e^{i\theta_1}$, $= R_2 e^{i\theta_2}$, $q^2 = Q e^{i\psi}$.

We thus get

$$\frac{r_1 + q^2 r_2}{1 + q^2 r_1 r_2} = \frac{R_1 e^{i\theta_1} + QR_2 e^{i(\theta_2 + \psi)}}{1 + QR_1 R_2 e^{i(\theta_1 + \theta_2 + \psi)}}.$$

The intensity of the reflected beam is, therefore,

$$I = \frac{R_1^2 + Q^2 R_2^2 + 2QR_1 R_2 \cos(\theta_2 + \psi - \theta_1)}{1 + Q^2 R_1^2 R_2^2 + 2QR_1 R_2 \cos(\theta_2 + \psi + \theta_1)}.$$

The numerator is the square of the resultant of two vectors, R_1 and QR_2 , inclined at an angle $\theta_2 + \psi - \theta_1$. If, then, there is to be absolute blackness anywhere we must have $I = 0$, so that $R_1 = QR_2$ and $\theta_2 + \psi - \theta_1 = (2n+1)\pi$ where n is an integer.

It will be necessary to distinguish two cases—first, when the angle of incidence is less than the critical angle of the glass, and second when it is greater than that angle. In each case vibrations parallel and perpendicular to the plane of incidence must be dealt with separately.

(A) *Below the Critical Angle.*

If ϕ be the angle of incidence, ϕ' that of refraction, and μ_1 the refractive index of the glass, we have $\sin \phi' = \mu_1 \sin \phi$. The surface of separation is $x = 0$, the plane of xy is that of incidence, so that everything is independent of z . The components of the light vector are proportional to $e^{i\psi[t - (x \cos \phi' + y \sin \phi')/V_1]}$ where V_1 is the velocity of light in air. Putting $x = c$ we see that $q = e^{-i(pc \cos \phi'/V_1)} = e^{-i(2\pi c/\lambda \cdot \cos \phi')}$ where λ is the wave-length in air. Hence we obtain $Q = 1$ and $\psi = -2\pi c/\lambda \cdot \cos \phi'$. We thus have

$$I = \frac{a + b \cos(\theta_2 + \psi - \theta_1)}{a_1 + b \cos(\theta_2 + \psi + \theta_1)},$$

where $a = R_1^2 + R_2^2$, $a_1 = 1 + R_1^2 R_2^2$, $b = 2R_1 R_2$.

For a given angle of incidence R_1 , R_2 , θ_1 , and θ_2 are constants and the only variable in the expression for I is ψ , which depends on the thickness (c) of the layer. Differentiating I with respect to ψ , we find that I is stationary when

$$b \sin 2\theta_1 + a \sin(\theta_1 + \theta_2 + \psi) + a_1 \sin(\theta_1 - \theta_2 - \psi) = 0;$$

$$\text{i.e., } (a - a_1) \cos \theta_1 \sin(\theta_2 + \psi) + (a + a_1) \sin \theta_1 \cos(\theta_2 + \psi) + b \sin 2\theta_1 = 0.$$

Putting $\tan \beta = \frac{a_1 + a}{a_1 - a} \tan \theta_1$ and $\sin \gamma = \frac{-b \sin 2\theta_1}{\sqrt{(a_1 - a)^2 + 4aa_1 \sin^2 \theta_1}}$ (it will appear from the sequel that γ is always real), we get

$$\sin(\psi + \theta_2 - \beta) = \sin \gamma.$$

$$\text{Thus } \psi + \theta_2 - \beta = n\pi + (-1)^n \gamma,$$

where n is any integer, so that

$$c = \frac{\lambda}{2\pi} \sec \phi' [m\pi + (-1)^m \gamma + \theta_2 - \beta],$$

m being an integer.

By giving different values to m we see that there will be rings of maximum and minimum intensity.

Light polarised perpendicularly to the Plane of Incidence.

If we suppose the transition from glass to air to be abrupt, then r_1 as given by Fresnel's formula; viz.,

$$r_1 = \frac{\tan(\phi - \phi')}{\tan(\phi + \phi')} = \frac{-\tan(\phi' - \phi)}{\tan(\phi' + \phi)}.$$

When ϕ lies between 0 and the polarising angle ($\tan^{-1} 1/\mu$), this gives

$$R_1 = \frac{\tan(\phi' - \phi)}{\tan(\phi' + \phi)} \quad \text{and} \quad \theta_1 = \pi$$

while when ϕ is greater than the polarising angle it gives

$$R_1 = \frac{\tan(\phi' - \phi)}{-\tan(\phi' + \phi)} \quad \text{and} \quad \theta_1 = 0.$$

In both cases I is stationary when $\theta_2 + \psi = n\pi$, n being an integer. The maximum value of I is

$$\frac{a+b}{a_1-b} = \left(\frac{R_1 + R_2}{1 + R_1 R_2} \right)^2,$$

and the minimum is

$$\frac{a-b}{a_1-b} = \left(\frac{R_1 - R_2}{1 - R_1 R_2} \right)^2.$$

When ϕ is less than the polarising angle I is a maximum when n is odd, and a minimum when n is even; when ϕ is greater than that angle I is a minimum when n is odd and a maximum when n is even. At the polarising angle $b = 0$ so that $I = a/a_1$ (a constant), and there are no rings.

If we suppose the transition from glass to air to be gradual and not abrupt, then we know that θ_1 enters by degrees instead of suddenly becoming π at the polarising angle. Except, however, within a few degrees of the polarising angle, r_1 is sufficiently well represented by Fresnel's formula above. In the immediate neighbourhood of the polarising angle we have

$$v_1 = x - iy \quad \text{where} \quad x = \frac{\tan(\phi - \phi')}{\tan(\phi + \phi')}, \quad \text{and} \quad y = \frac{\epsilon}{\cos \phi + \mu \cos \phi'},$$

ϵ being a small constant depending on the thickness of the layer of transition and the law of variation of the refractive index within that layer.* It thus appears that b will be a small quantity, and that $b \sin 2\theta_1$ will always be less than $\sqrt{(a_1 - a)^2 + 4aa_1 \sin^2 \theta_1}$ and that γ will be small. β , however, will not be small, but will vary from 0 to π , being 0 when $\theta_1 = 0$, $\frac{1}{2}\pi$ at the polarising angle, and π when θ_1 is π . I is a maximum when n is even, in which case its value is $\frac{a + b \cos(\theta_1 - \gamma - \beta)}{a_1 + b \cos(\theta_1 + \gamma + \beta)}$ and a minimum when n is odd,

in which case its value is $\frac{a - b \cos(\theta_1 + \gamma - \beta)}{a_1 - b \cos(\theta_1 - \gamma + \beta)}$. Owing to the smallness of

b the variations of intensity will be very slight, so that the rings in the neighbourhood of the polarising angle will scarcely be visible.

For the determination of the radii of the rings and their intensity nothing remains but the calculation of the constants R_1 , R_2 , θ_2 . For this purpose we shall take $\mu_1 = 1.596$, which gives a polarising angle of $32^\circ 1'$ and a critical angle of $38^\circ 47'$. We obtain R_1 from the formulæ already given.

* See 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 61.

ϕ .	R_1 .	ϕ .	R_1 .
0° 0'	0.2304	38° 0'	0.4541
10 0	0.2195	38 15	0.5257
20 0	0.1747	38 30	0.6248
30 0	0.0524	38 46	0.8812
35 0	0.1212		

R_2 and θ_2 are determined from the formula

$$R_2 e^{i\theta_2} = r_2 = \frac{\tan(\phi' - \phi'')}{\tan(\phi' + \phi'')},$$

where ϕ'' is a complex quantity given by $\sin \phi' = (\mu_0 - ia) \sin \phi''$. Here μ_0 is the "refractive index" of the metal, i.e., the ratio of the velocity of light in air to that in the metal, and a/μ_0 is the coefficient of absorption.

We shall put $\mu_0 - ia = M e^{-ia}$. For all the metals M^2 is large; according to Drude's experiments it is least for copper, where its value is 7.27, and greatest for zinc, where its value is 34.52. For the two metals—silver and steel—to which we shall apply the theory, M^2 is 13.5 and 17.37 respectively, so that the error in neglecting M^{-4} and higher powers of M^{-2} will be very small. To this order of approximation we have

$$\cos \phi'' = 1 - \frac{\sin^2 \phi'}{2M^2} e^{2ia}.$$

$$\begin{aligned} \frac{1 + R_2 e^{i\theta_2}}{1 - R_2 e^{i\theta_2}} &= (\mu_0 - ia) \cos \phi' \left[1 + \frac{\sin^2 \phi'}{2M^2} e^{2ia} \right] \\ &= \cos \phi' \left[\mu_0 \left(1 + \frac{\sin^2 \phi'}{2M^2} \right) - ia \left(1 - \frac{\sin^2 \phi'}{2M^2} \right) \right]. \end{aligned}$$

Therefore

$$R_2 e^{i\theta_2} = \frac{\cos \phi' [\mu_0 (1 + \sin^2 \phi' / 2M^2) - ia (1 - \sin^2 \phi' / 2M^2)] - 1}{\cos \phi' [\mu_0 (1 + \sin^2 \phi' / 2M^2) - ia (1 - \sin^2 \phi' / 2M^2)] + 1}.$$

Whence

$$R_2^2 = \frac{1-x}{1+x},$$

where

$$\begin{aligned} x &= \frac{2\mu_0 \cos \phi' (1 + \sin^2 \phi' / 2M^2)}{1 + M^2 \cos^2 \phi' [1 - (a^2 - \mu_0^2) \sin^2 \phi' / M^4 + \sin^4 \phi' / 4M^4]} \\ &= \frac{2\mu_0 \cos \phi' [1 + \sin^2 \phi' / 2M^2]}{1 + M^2 \cos^2 \phi' [1 + \sin^4 \phi' / 4M^4] + \sin^2 \phi' \cos^2 \phi' \cos 2\alpha}, \end{aligned}$$

and

$$\tan \theta_2 = - \frac{2a \cos \phi' [1 - \sin^2 \phi' / 2M^2]}{-1 + M^2 \cos^2 \phi' [1 + \sin^4 \phi' / 4M^4] + \sin^2 \phi' \cos^2 \phi' \cos 2\alpha}.$$

By the aid of these formulæ the following values of R_2 and θ_2 have been calculated for silver and steel.

Silver.

$$\mu_0 = 0.18; a = 3.67; M^2 = 13.5;$$

$$\cos \alpha = -0.9952.$$

ϕ .	ϕ' .	R_1^2 .	R_2 .	θ_2 .
0 0	0 0	0.952	0.976	329 35
10 0	16 9	0.960	0.975	328 18
20 0	33 6	0.942	0.971	328 39
30 0	52 57	0.925	0.962	310 24
35 0	66 17	0.907	0.953	290 10
38 0	79 19	0.908	0.953	249 0
38 15	81 12	0.916	0.957	236 52
38 30	83 30	0.930	0.965	223 38
38 46	88 14	0.969	0.989	192 26

Steel.

$$\mu_0 = 2.41; a = 3.40; M^2 = 17.37;$$

$$\cos \alpha = -0.3283.$$

ϕ .	R_1^2 .	R_2 .	θ_2 .
0 0	0.585	0.764	337 26
10 0	0.576	0.759	336 41
20 0	0.502	0.709	333 5
30 0	0.429	0.655	322 26
35 0	0.320	0.566	303 18
38 0	0.267	0.517	251 20
38 15	0.297	0.545	239 17
38 30	0.370	0.608	223 46
38 46	0.738	0.859	191 42

We are now in a position to calculate the intensity I at any point. For our purposes it will be sufficient to determine the maximum and minimum values of I and its values at and very near the centre. We have already seen (p. 519) that the maximum value of I is $\left(\frac{R_1 + R_2}{1 + R_1 R_2}\right)^2$, and the minimum $\left(\frac{R_1 - R_2}{1 - R_1 R_2}\right)^2$.

Very near the centre $\psi = 0$, and we have

$$I = \frac{a - b \cos \theta_2}{a_1 - b \cos \theta_2},$$

where ϕ is less than the polarising angle, and

$$I = \frac{a + b \cos \theta_2}{a_1 + b \cos \theta_2},$$

where ϕ is greater than that angle.

From these formulæ and the numerical results on pp. 520 and 521 the following table has been made up:—

Silver.

ϕ .	I (max.).	I (min.).	I (near centre).
0 0	0.969	0.924	0.931
10 0	0.967	0.923	0.930
20 0	0.958	0.918	0.928
30 0	0.932	0.917	0.921
35 0	0.926	0.882	0.916
38 0	0.962	0.773	0.914
38 15	0.974	0.753	0.913
38 30	0.982	0.732	0.914
38 46	0.998	0.704	0.915

Steel.

ϕ .	I (max.).	I (min.).	I (near centre).
0 0	0.715	0.420	0.442
10 0	0.708	0.419	0.441
20 0	0.618	0.372	0.393
30 0	0.468	0.390	0.398
35 0	0.413	0.238	0.380
38 0	0.619	0.007	0.367
38 15	0.692	0.001	0.356
38 30	0.798	0.001	0.355
38 46	0.981	0.008	0.354

The value of the intensity at the centre cannot be obtained from these formulæ, for at that point there is no air space between the glass and metal, so that we have direct reflection from the metal. The intensity in this case can be obtained from the formula for R_s^2 on p. 520 by replacing μ_0 and a by μ_0/μ_1 and a/μ_1 respectively. In this way we obtain the following values of the intensity for different values of ϕ ranging from 0 to 90° .

ϕ .	0° .	10° .	20° .	30° .	40° .	50° .	60° .	70° .	80° .	90° .
(Silver) I...	0.931	0.930	0.929	0.924	0.918	0.910	0.905	0.896	0.925	1
(Steel) I...	0.442	0.438	0.425	0.406	0.362	0.316	0.266	0.215	0.246	1

The radii of the rings can be readily obtained. If r be the radius of a ring, κ the curvature of the lens, we have very approximately $c = \frac{1}{2}\kappa r^2$. We have seen that at any point on a ring of maximum or minimum intensity

$$\psi + \theta_2 = n\pi; \quad \psi = -\frac{2\pi c}{\lambda} \cos \phi' = \frac{\pi \kappa r^2}{\lambda} \cos \phi'.$$

Hence we have

$$\rho = r \sqrt{\frac{\kappa}{\lambda}} = \sqrt{\left(\frac{\theta_2}{\pi} - n\right) \sec \phi'}.$$

The smallest ring corresponds to $n = 1$, the next to $n = 0$, the next to $n = -1$ and so on. From this formula we shall calculate the values of ρ_1 , ρ_2 , ρ_3 , and ρ_4 (corresponding to the first four rings), for different values of ϕ ranging from zero to the critical angle.

Silver.

ϕ .	ρ_1 .	ρ_2 .	ρ_3 .	ρ_4 .
$0^\circ 0'$	0.912	1.35	1.68	1.96
$10^\circ 0'$	0.925	1.38	1.71	2.00
$20^\circ 0'$	0.976	1.47	1.83	2.18
$30^\circ 0'$	1.10	1.69	2.13	2.48
$35^\circ 0'$	1.23	2.00	2.55	3.00
$38^\circ 0'$	1.41	2.72	3.58	4.26
$38^\circ 15'$	1.44	2.93	3.89	4.66
$38^\circ 30'$	1.463	3.31	4.45	5.35
$38^\circ 46'$	1.466	5.89	8.19	9.98
$38^\circ 47'$	1.5	∞	∞	∞

Steel.

ϕ .	ρ_1 .	ρ_2 .	ρ_3 .	ρ_4 .
$0^\circ 0'$	0.935	1.37	1.70	1.97
$10^\circ 0'$	0.952	1.40	1.73	2.01
$20^\circ 0'$	1.01	1.53	1.88	2.17
$30^\circ 0'$	1.15	1.72	2.15	2.51
$35^\circ 0'$	1.31	2.05	2.58	3.03
$38^\circ 0'$	1.43	2.73	3.59	4.27
$38^\circ 15'$	1.44	2.95	3.90	4.67
$38^\circ 30'$	1.45	3.31	4.45	5.35
$38^\circ 46'$	1.45	5.88	8.19	9.97
$38^\circ 47'$	1.45	∞	∞	∞

From these results it will appear that the rings open out as the angle of incidence increases. The expansion of all the rings except the first is very rapid when nearing the critical angle, and the radius of each increases to

infinity when the critical angle is reached. With the first ring, however, there is very little change as the critical angle is approached, and the limiting value of $r\sqrt{\kappa/\lambda}$ is 1.5 for silver and 1.45 for steel. Our formulæ cannot, in strictness, be applied when ϕ is exactly equal to the critical angle, for then $|q^2 r_2 r_3| = 1$, and the fundamental series on p. 517 loses its convergence. We may, however, approach the critical angle as near as we wish. We have seen that

$$\tan \theta_2 = -\frac{2a \cos \phi' [1 - \sin^2 \phi' / 2M^2]}{M^2 \cos^2 \phi' [1 + \sin^4 \phi' / 4M^4] + \sin^2 \phi' \cos^2 \phi' \cos 2a - 1}.$$

When ϕ' is nearly 90° , $\tan \theta_2$ is very small, and we have

$$\theta_2 - \pi = \tan(\theta_2 - \pi) \text{ approx.}$$

Therefore

$$(\theta_2 - \pi) \sec \phi' = \frac{-2a [1 - \sin^2 \phi' / 2M^2]}{M^2 \cos^2 \phi' [1 + \sin^4 \phi' / 4M^4] + \sin^2 \phi' \cos^2 \phi' \cos 2a - 1},$$

the limit of which is $2a(1 - 1/2M^2)$. Whence

$$\begin{aligned} \rho_1 &= \sqrt{\left(\frac{\theta_2}{\pi} - 1\right) \sec \phi'} \\ &= \sqrt{\frac{2a}{\pi} (1 - 1/2M^2)}, \end{aligned}$$

which gives the values for silver and steel recorded above.

From the formula

$$r \sqrt{\frac{\kappa}{\lambda}} = \sqrt{\left(\frac{\theta_2}{\pi} - n\right) \sec \phi'}$$

we see that r is a function of λ , so that, unless homogeneous light be employed, the rings will be coloured. ϕ' and consequently θ_2 are functions of λ , but the change in r due to this fact will be inappreciable, and very approximately we shall have $r \propto \sqrt{\lambda}$. Thus, if r_a , r_d , and r_h be radii corresponding to Fraunhofer's lines A, D, and H in the spectrum, A being in the extreme red and H in the violet, we have, approximately,

$$\frac{r_a}{r_d} = \sqrt{\frac{\lambda_a}{\lambda_d}} = \sqrt{\frac{76}{59}} = 1.14,$$

and

$$\frac{r_h}{r_d} = \sqrt{\frac{\lambda_h}{\lambda_d}} = \sqrt{\frac{39}{59}} = 0.81.$$

In what way this will affect the appearance of the rings will be seen most clearly by drawing curves to represent the intensity for various angles of incidence. The following tables give the value of ρ corresponding to the lines

A, D, and H, the values of ρ in the tables on p. 522 being taken to correspond to the line D:—*

Silver.

ϕ .	0°.	20°.	35°.
First ring	ρ_h	0·741	0·793
	ρ_d	0·912	0·976
	ρ_a	1·04	1·11
Second "	ρ_h	1·10	1·19
	ρ_d	1·35	1·47
	ρ_a	1·53	1·67
Third "	ρ_h	1·37	1·49
	ρ_d	1·68	1·83
	ρ_a	1·91	2·06
Fourth "	ρ_h	1·59	1·73
	ρ_d	1·96	2·13
	ρ_a	2·23	2·43

Steel.

ϕ .	0°.	20°.	35°.
First ring	ρ_h	0·760	0·821
	ρ_d	0·935	1·01
	ρ_a	1·06	1·15
Second "	ρ_h	1·11	1·24
	ρ_d	1·37	1·53
	ρ_a	1·56	1·74
Third "	ρ_h	1·38	1·53
	ρ_d	1·70	1·88
	ρ_a	1·93	2·13
Fourth "	ρ_h	1·60	1·76
	ρ_d	1·97	2·17
	ρ_a	2·24	2·46

The general effect of this dependence of the radius on the wave-length will be that each bright ring will change in colour from violet on the inside to red on the outside, whereas in the dark rings the order of colours will be reversed. As, however, in the case of silver, the difference between the maximum and minimum intensities is nowhere great, the rings will not be conspicuous enough to show the colours well. Another effect, well illustrated by the

* These results, however, neglect the change in the optical constants of the metals with changing wave-length, so can only be considered as illustrative for metals of the various types. The ring system has in fact been employed by P. Glau to determine the phase-change on reflection for different colours.

tables above, is that—for all the rings except the first—the red of one ring will overlap the violet of the next. This will diminish the sharpness of the rings, and make the first appear more conspicuous than the others.

Following Stokes, we shall compare these results with the case when the metal is replaced by glass of the same refractive index as the first piece. The phenomena in this case are very well known and have been frequently discussed mathematically. We have only to put $r_2 = r_3 = -r_1$ and $q^2 = e^{i\psi}$ in the formulæ of p. 517, and we get for the reflected beam

$$\frac{R_1 e^{i\theta_1} (1 - e^{i\psi})}{1 - R_1^2 e^{i(\psi + 2\theta_1)}}.$$

Except near the polarising angle we may put $\theta_1 = 0$ or π , so that $e^{i2\theta_1} = 1$, and we get

$$I = \frac{4R_1^2 \sin^2 \frac{1}{2}\psi}{1 + R_1^4 - 2R_1^2 \cos \psi}.$$

This has maxima and minima when $\psi = n\pi$, where n is an integer. If n is even, $I = 0$, and if n is odd, $I = 4R_1^2/(1 + R_1^2)^2$.

The radii are given by $r\sqrt{\kappa/\lambda} = \sqrt{n \sec \phi'}$. Where $n = 0$, we get $r = 0$ and $I = 0$, so that there is a black spot at the centre. The following table gives the value of $r\sqrt{\kappa/\lambda}$ for the first four rings corresponding to $n = 1, 2, 3, 4$ respectively, the first one being bright.

Glass.

ϕ .	ρ_1 .	ρ_2 .	ρ_3 .	ρ_4 .
0 0	1.00	1.41	1.73	2.00
10 0	1.02	1.44	1.77	2.04
20 0	1.09	1.55	1.89	2.19
30 0	1.29	1.82	2.23	2.58
35 0	1.58	2.23	2.73	3.15
38 0	2.32	3.29	4.02	4.65
38 15	2.56	3.62	4.43	5.11
38 30	2.97	4.20	5.15	5.94
38 46	5.70	8.06	9.87	11.4
38 47	∞	∞	∞	∞

The maximum value of I , i.e., its value at the first, third, etc., ring is as follows:—

ϕ .	0°.	10°.	20°.	30°.	35°.	38°.	38° 15'.	38° 30'.	38° 46'.
(Max.) I ...	0.438	0.419	0.339	0.105	0.239	0.567	0.678	0.808	0.984

To exhibit the influence of colour on the size of the rings we have the following table:—

Glass.

ϕ .		0°.	20°.	33°.
First ring	ρ_h	0·81	0·886	1·89
	ρ_d	1·00	1·09	2·32
	ρ_a	1·14	1·24	2·63
Second "	ρ_h	1·15	1·26	2·68
	ρ_d	1·41	1·55	3·29
	ρ_a	1·60	1·76	3·73
Third "	ρ_h	1·41	1·54	3·27
	ρ_d	1·73	1·89	4·02
	ρ_a	1·96	2·14	4·56
Fourth "	ρ_h	1·63	1·78	3·78
	ρ_d	2·00	2·19	4·65
	ρ_a	2·27	2·48	5·28

It will be well to illustrate most of these matters graphically. Figs. 1, 2, 3, and 4 represent the first four rings for values of ϕ (0°, 10°, 20°, and 30°)

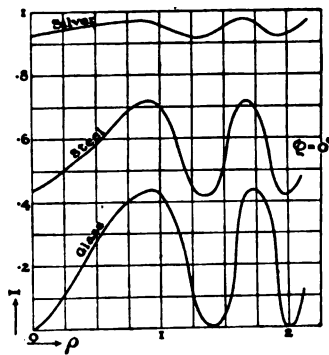


FIG. 1.

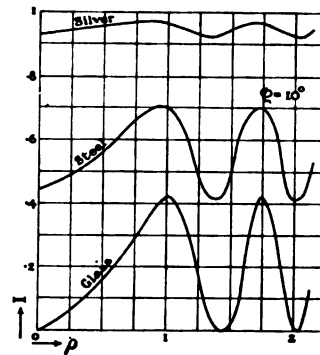


FIG. 2.

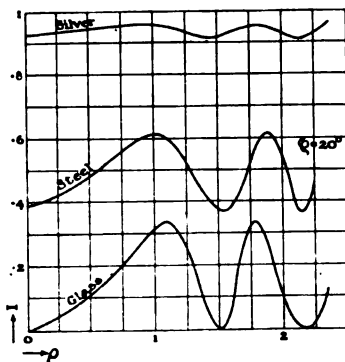


FIG. 3.

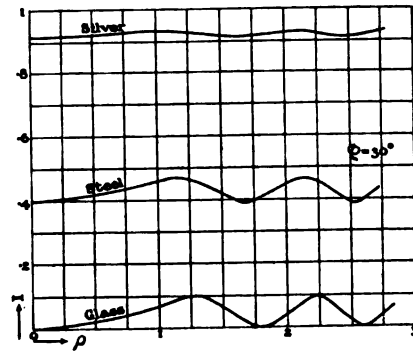


FIG. 4.

below the polarising angle. A glance at these figures will show that the rings are all dark-centred, that they gradually expand as ϕ increases, and that the rings are much less distinct with silver than with steel or glass. The rings are most distinct with glass, but the difference between that and steel is not very marked.

Fig. 4 shows that as the polarising angle is approached the rings rapidly disappear. After passing the polarising angle the rings pass from dark-centred to bright-centred in the case of the metals; but with glass they remain bright-centred throughout. This is clearly brought out in figs. 5, 6, 7, and 8 which follow. The rings are still very much more distinct with glass and steel than with silver. There is a close resemblance between the rings with glass and with steel—the main difference being that the rings with steel are bright-centred, but the brightness at the centre is not very appreciable compared with that at the rings. The rings with steel are slightly more distinct than with glass and slightly larger. After passing the polarising angle the rings have all expanded so much that it is convenient to use a smaller scale for represent the radius, and in the figures that follow (5 to 8) the scale of ρ is half that in the earlier figures.

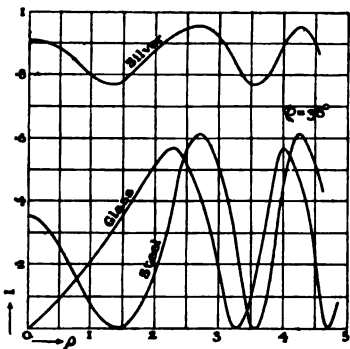


FIG. 5.

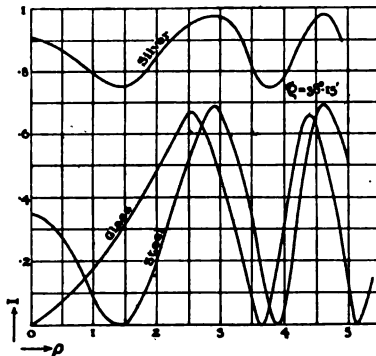


FIG. 6.

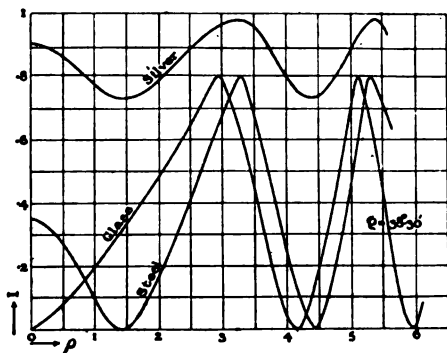


FIG. 7.

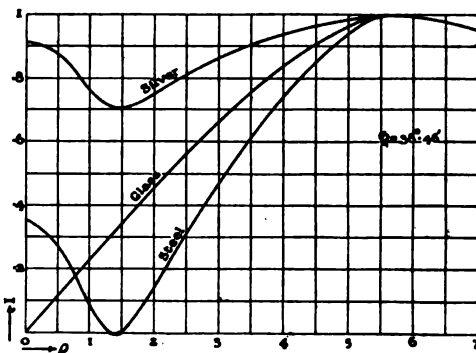


FIG. 8.

The colour effects are brought out by figs. 9 and 10, the first of which deals with the case where $\phi = 0$ and the second with $\phi = 38^\circ$, i.e., beyond the polarising angle. The dotted curve represents the intensity for red, and the continuous curve that for violet.

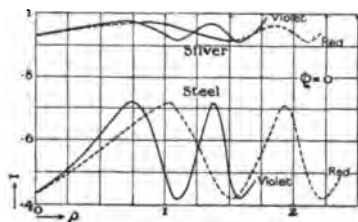


FIG. 9.

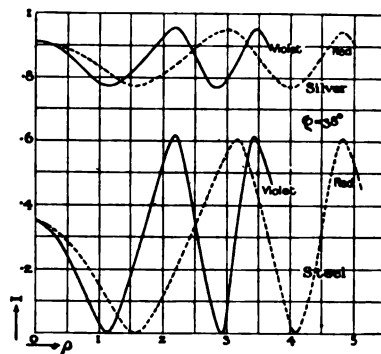


FIG. 10.

Light Polarised Parallel to the Plane of Incidence.

In this case the influence of the transition layer on the phase is always very small, so that we may employ Fresnel's formula throughout and put

$$r_1 = \frac{\sin(\phi' - \phi)}{\sin(\phi' + \phi)} = R_1 \quad \text{and} \quad \theta_1 = 0.$$

We then (see p. 518) have

$$I = \frac{a + b \cos(\theta_2 + \psi)}{a_1 + b \cos(\theta_2 + \psi)};$$

so that maxima and minima occur when $\theta_2 + \psi = n\pi$, n being any integer. The maximum intensity is

$$\frac{a+b}{a_1+b} = \left(\frac{R_1 + R_2}{1 + R_1 R_2} \right)^2,$$

and the minimum is

$$\frac{a-b}{a_1-b} = \left(\frac{R_1 - R_2}{1 - R_1 R_2} \right)^2.$$

The rings will be dark-centred throughout, instead of passing from dark-centred to bright-centred as with light polarised perpendicularly to the plane of incidence.

We have the following values of R_1 obtained from the formula above:—

ϕ .	R_1 .	ϕ .	R_1 .
0° 0'	0.230	38° 0'	0.743
10 0	0.243	38 15	0.783
20 0	0.283	38 30	0.834
30 0	0.393	38 46	0.952
35 0	0.530		

R_2 and θ_2 are determined from the formula (cf. p. 520).

$$R_2 e^{i\theta_2} = r_2 = \frac{\sin(\phi'' - \phi')}{\sin(\phi'' + \phi')}.$$

This makes

$$\frac{1 - R_2 e^{i\theta_2}}{1 + R_2 e^{i\theta_2}} = \frac{\sin \phi' \cos \phi''}{\cos \phi' \sin \phi''}.$$

whence

$$R_2 e^{i\theta_2} = \frac{1 - \mu_0 (1 - \sin^2 \phi' / 2M^2) \sec \phi' + i\alpha (1 + \sin^2 \phi' / 2M^2) \sec \phi'}{1 + \mu_0 (1 - \sin^2 \phi' / 2M^2) \sec \phi' - i\alpha (1 + \sin^2 \phi' / 2M^2) \sec \phi'}.$$

which gives

$$R_2^2 = \frac{1 - x}{1 + x},$$

where

$$\begin{aligned} x &= \frac{2\mu_0 \sec \phi' (1 - \sin^2 \phi' / 2M^2)}{1 + M^2 \sec^2 \phi' [1 + M^{-4} (\alpha^2 - \mu_0^2) \sin^2 \phi' + 4M^{-4} \sin^4 \phi']} \\ &= \frac{2\mu_0 \sec \phi' (1 - \sin^2 \phi' / 2M^2)}{1 + M^2 \sec \phi' (1 + \sin^2 \phi' / 2M^2) - \tan^2 \phi' \cos 2\alpha}, \end{aligned}$$

and

$$\begin{aligned} \tan \theta_2 &= \frac{-2\alpha \sec \phi' (1 + \sin^2 \phi' / 2M^2)}{M^2 \sec^2 \phi' - 1 + M^{-2} \tan^2 \phi' (\alpha^2 - \mu_0^2 + \frac{1}{4} \sin^2 \phi')} \\ &= \frac{-2\alpha \sec \phi' (1 + \sin^2 \phi' / 2M^2)}{-1 + M^2 \sec^2 \phi' (1 + \sin^2 \phi' / 2M^2) - \tan^2 \phi' \cos 2\alpha}. \end{aligned}$$

By the aid of these formulæ the following values of R_2 and θ_2 have been obtained:—

Silver.

ϕ .	R_2^2 .	R_2 .	θ_2 .
0° 0'	0.952	0.976	329° 35'
10 0	0.953	0.976	330 48
20 0	0.959	0.980	334 36
30 0	0.971	0.985	341 49
35 0	0.985	0.992	349 52
38 0	0.992	0.996	354 25
38 47	1.000	1.000	360 0

Steel.

ϕ .	R_2^2 .	R_2 .	θ_2 .
0° 0'	0.585	0.764	327° 26'
10 0	0.597	0.773	336 21
20 0	0.639	0.799	341 12
30 0	0.726	0.852	348 23
35 0	0.830	0.911	353 0
38 0	0.907	0.952	355 48
38 47	1.000	1.000	360 0

From these results we derive the following values for the intensity at the bright and dark rings, and near the centre (*cf.* p. 521):—

Silver.

ϕ .	I (max.).	I (min.).	I (near centre).
0 0	0.969	0.924	0.931
10 0	0.971	0.924	0.930
20 0	0.976	0.929	0.935
30 0	0.987	0.935	0.941
35 0	0.996	0.949	0.953
38 0	0.999	0.959	0.963
38 46	1.000	1.000	1.000

Steel.

ϕ .	I (max.).	I (min.).	I (near centre).
0 0	0.715	0.420	0.442
10 0	0.731	0.426	0.452
20 0	0.779	0.445	0.467
30 0	0.869	0.476	0.497
35 0	0.945	0.542	0.644
38 0	0.987	0.551	0.986
38 46	1.000	1.000	1.000

The value of the intensity at the centre (*cf.* p. 521) is obtained from the formula for R_2^2 on p. 529 by replacing μ_0 and a by μ_0/μ_1 and a/μ_1 respectively. In this way we obtain the following values of the intensity as ϕ ranges from 0 to 90° :—

ϕ .	0° .	10° .	20° .	30° .	40° .	50° .	60° .	70° .	80° .	90° .
I (silver)...	0.931	0.932	0.936	0.941	0.949	0.957	0.967	0.978	0.989	1
I (steel) ...	0.443	0.449	0.467	0.484	0.541	0.600	0.674	0.765	0.873	0

For the radii of the rings we have the following values (*cf.* p. 522):—

Silver.

ϕ .	p_1 .	p_2 .	p_3 .	p_4 .
0 0	0.912	1.35	1.68	1.96
10 0	0.934	1.39	1.72	2.00
20 0	1.01	1.49	1.85	2.15
30 0	1.22	1.99	2.19	2.54
35 0	1.53	2.20	2.71	3.13
38 0	2.29	3.26	3.91	4.63
38 47	∞	∞	∞	∞

Steel.

ϕ .	p_1 .	p_2 .	p_3 .	p_4 .
0 0	0.935	1.37	1.70	1.97
10 0	0.957	1.40	1.73	2.01
20 0	1.03	1.50	1.86	2.16
30 0	1.24	1.79	2.20	2.55
35 0	1.55	2.21	2.71	3.14
38 0	2.30	3.27	4.01	4.63
38 47	∞	∞	∞	∞

The influence of colour on the size of the rings is exhibited in the following tables:—

Silver.

ϕ .	0°.	20°.	38°.
First ring	ρ_h	0·741	0·821
	ρ_d	0·912	1·01
	ρ_a	1·04	1·15
Second "	ρ_h	1·10	1·21
	ρ_d	1·35	1·49
	ρ_a	1·53	1·69
Third "	ρ_h	1·37	1·50
	ρ_d	1·68	1·85
	ρ_a	1·91	2·10
Fourth "	ρ_h	1·59	1·75
	ρ_d	1·96	2·15
	ρ_a	2·23	2·44

Steel.

ϕ .	0°.	20°.	38°.
First ring	ρ_h	0·760	0·837
	ρ_d	0·935	1·03
	ρ_a	1·06	1·17
Second "	ρ_h	1·11	1·22
	ρ_d	1·37	1·50
	ρ_a	1·55	1·70
Third "	ρ_h	1·38	1·51
	ρ_d	1·70	1·86
	ρ_a	1·93	2·11
Fourth "	ρ_h	1·60	1·76
	ρ_d	1·97	2·16
	ρ_a	2·24	2·45

If we wish to compare these results with those for glass we have merely to substitute the values of R_1 in the formula of p. 525. The radii of the rings are the same as for the case of perpendicularly-polarised light. The only difference is that the maximum value of I is now given by the following table:—

ϕ .	0°.	10°.	20°.	30°.	35°.	38°.	38° 47'.
(Max.) I ...	0·438	0·459	0·525	0·690	0·827	0·958	1

The graphical representation of these results is undertaken in the next three figures. It will be seen that the rings with silver are very indistinct.

With steel, however, the rings begin, when ϕ is small, by being almost as marked as with glass. They remain fairly distinct as ϕ increases, but the rings with glass gain in intensity much more markedly than with steel. In all cases the rings are dark-centred; but, as will be seen from fig. 13, as we approach the critical angle the difference between the intensity at the centre and at the first ring is—with the metals—very slight, so that there will appear to be a bright spot at the centre.

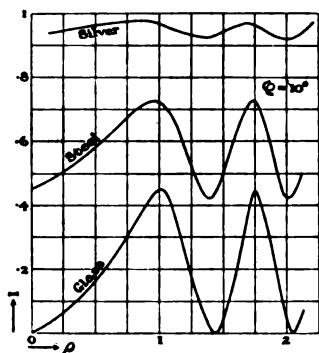


FIG. 11.

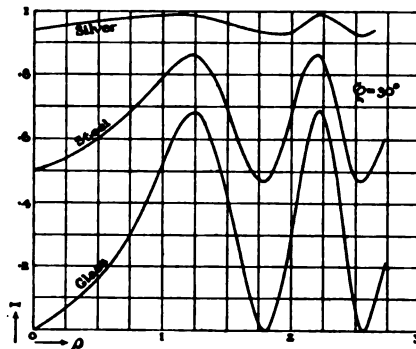


FIG. 12.

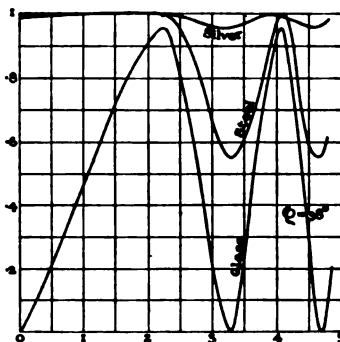
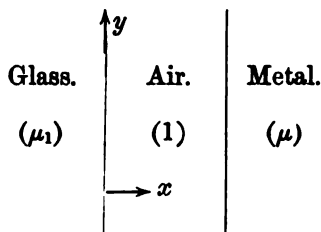


FIG. 13.

(B) *Beyond the Critical Angle.*

Before we can proceed beyond the critical angle it will be necessary to discuss briefly the reflection and refraction of the "surface waves" due to total reflection.



Supposing light to be due to displacements in a rotational ether, we have the following expressions for the kinetic energy and work function in an isotropic medium :—

$$T = \frac{1}{2} \int \rho (\xi^2 + \eta^2 + \zeta^2) dV;$$

$$W = \frac{1}{2} c_1^2 \int \rho \mu^2 (f^2 + g^2 + h^2) dV.$$

Here dV is an element of volume, ρ the density, $\xi\eta\zeta$ the displacement $(fgh) = 1/\mu^2 \cdot \text{curl}(\xi\eta\zeta)$, c_1 the velocity of light in free ether, μ a constant which represents the refractive index in the case of a transparent medium. The dynamical equations and boundary conditions are most simply obtained from the Principle of Action, which makes $\delta \int (T - W) dt = 0$. This leads at once to three dynamical equations of the form $\ddot{\xi} = c_1^2 \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right)$, and shows that the boundary conditions are satisfied if $\rho c_1^2 (ng - mh)$, $\rho c_1^2 (lh - nf)$, $\rho c_1^2 (mf - lg)$ are continuous, where (lmn) are the direction cosines of the outward normal to the bounding surface. The displacement $(\xi\eta\zeta)$ must also be continuous to avoid rupture of the material. We take (f, g, h) to represent the light vector. The surface of separation is $x = 0$, the plane of xy is that of incidence, so that everything is independent of z .

Light Polarised Perpendicularly to the Plane of Incidence.

In this case (f, g, h) is a vector *parallel* to the plane of incidence, so that (ξ, η, ζ) is at right angles to that plane.

Thus $\xi = 0 = \eta$.

In the glass

$$\zeta = e^{ip[(x \cos \phi + y \sin \phi)/V - t]} \quad (\text{incident})$$

$$+ r_1 e^{ip[(-x \cos \phi + y \sin \phi)/V - t]} \quad (\text{reflected}).$$

In the air

$$\zeta = \frac{s_1}{\mu_1} e^{ip[(x + y \sin \phi)/V - t]} \quad (\text{refracted}),$$

where V is the velocity of light in the glass. The amplitudes of the three waves are in the ratio $1 : |r_1| : |s_1|$.

The dynamical equations require that $n^2 + \sin^2 \phi / V^2 = 1/V_1^2$. Therefore

$$n = +i\sqrt{\sin^2 \phi - 1/\mu_1^2},$$

the sign of the radical being chosen so as to make ζ diminish as x increases.

The boundary conditions give

$$1 + r_1 = \frac{s_1}{\mu_1}, \quad \text{and} \quad 1 - r_1 = \frac{n\mu_1 s_1}{\cos \phi} = -i \frac{s_1}{\mu_1} \tan \frac{\theta_1}{2},$$

where

$$\tan \frac{\theta_1}{2} = -\frac{\mu_1^2 \sqrt{\sin^2 \phi_1 - 1/\mu_1^2}}{\cos \phi}$$

From these we get

$$r_1 = e^{i\theta_1} \text{ (so that } R_1 = 1).$$

This result could also be obtained by transforming Fresnel's formula $r_1 = \frac{\tan(\phi - \phi')}{\tan(\phi + \phi')}$ where ϕ' is complex and given by the equation $\sin \phi' = \mu_1 \sin \phi$. Moreover, from the above we derive $s_1 = 2\mu_1 \cos \frac{1}{2}\theta_1 e^{i\frac{1}{2}\theta_1}$. In exactly the same way, by considering a wave going from air to glass, we could prove that $r_3 = -e^{i\theta_1}$ and $s_3 = -\frac{2}{\mu_1} \sin \frac{1}{2}\theta_1 e^{i(\theta_1 + \pi)}$. Hence, $r_1 + r_3 = 0$ and $s_1 s_3 = 1 - r_1^2$ in accordance with the statement on p. 517.

The following table gives the values of θ_1 obtained from the formula

$$\tan \frac{\theta_1}{2} = -\frac{\mu_1^2 \sqrt{\sin^2 \phi_1 - 1/\mu_1^2}}{\cos \phi},$$

as ϕ increases from the critical angle:—

ϕ .	38° 47'.	38° 50'.	38° 55'.	39°.	39° 9'.	40°.
$-\theta_1 \dots$	0	9° 54'	17° 51'	22° 34'	29° 14'	51° 16'

ϕ .	45°.	50°.	60°.	70°.	80°.	90°.
$-\theta_1 \dots$	99° 32'	120° 24'	143° 40'	158° 8'	169° 46'	180°

To determine R_2 and θ_2 we have to consider a wave going from air to metal. In the air we have

$$\begin{aligned} \zeta &= e^{ip[(nx+y \sin \phi)/V-t]} \text{ (incident)} \\ &+ r_2 e^{ip[(-nx+y \sin \phi)/V-t]} \text{ (reflected).} \end{aligned}$$

In the metal,

$$\zeta = \frac{\mu^2}{\mu_0} s_2 e^{ip[(mx+y \sin \phi)/V-t]} \text{ (refracted),}$$

where

$$\mu = \mu_0 - ia;$$

n has the same value as before, and to satisfy the dynamical equations we must have

$$m^2 + \sin^2 \phi = V^2/V_0^2 = (\mu_0/\mu_1)^2,$$

V_0 being the velocity of propagation in the metal.

Thus

$$m^2 = (\mu_0/\mu_1)^2 - \sin^2 \phi.$$

There will be two distinct cases to discuss. For metals of one class (such as silver) $\mu_0/\mu_1 < \sin \phi$, so that m is imaginary. For metals of another class (such as steel) $\mu_0/\mu_1 > \sin \phi$, and m is real.

We shall first take the class to which silver belongs.

In this case

$$m = i\sqrt{\sin^2 \phi - (\mu_0/\mu_1)^2}$$

and

$$\frac{m}{n} = \sqrt{\frac{\sin^2 \phi - (\mu_0/\mu_1)^2}{\sin^2 \phi - (1/\mu_1)^2}} = \gamma, \text{ say.}$$

The boundary conditions give

$$1 + r_2 = \frac{\mu^2}{\mu_0} s_2, \text{ and } 1 - r_2 = \frac{m}{n} \frac{s_2}{\mu_0} = \frac{\gamma}{\mu^2} \frac{\mu^2}{\mu_0} s_2,$$

whence

$$r_2 = \frac{\mu^2/\gamma - 1}{\mu^2/\gamma + 1}.$$

This leads at once to

$$R_2^2 \frac{1+x}{1-x} \quad \text{where } x = \frac{-2M^2/\gamma \cos 2\alpha}{(M^2/\gamma)^2 + 1}$$

and

$$\tan \theta_2 = \frac{-2M^2/\gamma \sin 2\alpha}{(M^2/\gamma)^2 - 1}.$$

R_2 is greatest when $M^2/\gamma = 1$, in which case $x = -\cos 2\alpha$,

$R_2 = \tan \alpha = a/\mu_0$, and $\tan \theta_2$ is infinite.

These formulæ lead to the following values of R_2 and θ_2 :—

Silver.

ϕ .	R_2^2 .	R_2 .	θ_2 .	ϕ .	R_2^2 .	R_2 .	θ_2 .
38 47	1.00	1.00	0 0	45 0	1.88	1.37	178 11
38 50	13.6	3.69	9 39	50 0	1.67	1.29	178 38
38 55	41.6	20.4	90 0	60 0	1.53	1.24	178 48
39 0	45.8	6.73	174 38	70 0	1.48	1.22	178 53
40 0	3.82	1.95	175 57	80 0	1.46	1.21	178 55

In the case of a metal, like steel, for which $\mu_0/\mu_1 > 1$, m is real, and we get $m = +\mu_0/\mu_1 \cos \phi_1$ where ϕ_1 is a real angle determined by the relation $\sin \phi_1 = \mu_1/\mu_0 \sin \phi$ (so that ϕ_1 is less than ϕ).

Putting

$$\gamma' = \sqrt{\frac{(\mu_0/\mu_1)^2 - \sin^2 \phi}{\sin^2 \phi - (1/\mu_1)^2}} = \frac{\mu_0/\mu_1 \cdot \cos \phi_1}{\sqrt{\sin^2 \phi - (1/\mu_1)^2}},$$

the boundary conditions give

$$1 + r_2 = \frac{\mu^2}{\mu_0} s_2 \text{ and } 1 - r_2 = \frac{m}{n} \frac{s_2}{\mu_0} = -i\gamma' \frac{s_2}{\mu_0},$$

whence

$$r_2 = \frac{\mu^2/\gamma' + i}{\mu^2/\gamma' - i}.$$

This gives $R_2^2 = \frac{1+x}{1-x}$, where $x = \frac{2(M^2/\gamma') \sin 2\alpha}{(M^2/\gamma')^2 - 1}$

and $\tan \theta_2 = \frac{2(M^2/\gamma') \cos 2\alpha}{(M^2/\gamma')^2 - 1}.$

R_2 is greatest when

$$\frac{M^2}{\gamma'} = 1, \text{ in which case } x = \sin 2\alpha, \quad R_2 = \frac{1 + \tan \alpha}{1 - \tan \alpha} = \frac{a + \mu_0}{a - \mu_0},$$

and $\tan \theta_2$ is infinite.

From these results we derive the following table:—

Steel.

ϕ .	R_2^2 .	R_2 .	θ_2 .
38 47	1.00	1.00	0 0
39 0	21.8	4.67	51 21
39 9	34.5	5.87	90 0
40 0	8.67	2.94	152 48
45 0	2.44	1.56	170 41
50 0	1.91	1.38	178 23
60 0	1.57	1.25	175 26
70 0	1.45	1.20	176 17
80 0	1.39	1.18	176 41

In the formula on p. 517 we found

$$I = \frac{R_1^2 + Q^2 R_2^2 + 2QR_1 R_2 \cos(\theta_2 + \psi - \theta_1)}{1 + Q^2 R_1^2 R_2^2 + 2QR_1 R_2 \cos(\theta_2 + \psi + \theta_1)}$$

In the present case we have $R_1 = 1$, $\psi = 0$,

$$Q = e^{-4\pi r/\lambda} \cdot \sqrt{\sin^2 \phi - (1/\mu_1^2)} = e^{-2\pi r^2/\lambda} \cdot \sqrt{\sin^2 \phi - 1/\mu_1^2},$$

where, as before, r is the distance from the centre.

We thus have

$$I = \frac{1 + Q^2 R_2^2 + 2QR_2 \cos(\theta_2 - \theta_1)}{1 + Q^2 R_2^2 + 2QR_2 \cos(\theta_2 + \theta_1)}.$$

The numerator is the square of the resultant of two vectors 1 and QR_2 inclined at an angle $\theta_2 - \theta_1$. This resultant will always be least when $\theta_2 - \theta_1 = \pi$, and its least value will be zero if $1 = QR_2$. Hence, if we are seeking for places of absolute blackness we must take $\theta_2 - \theta_1 = \pi$ and $1 = QR_2$. The former condition, if it can be satisfied at all, will confine us to a particular angle of incidence ϕ ; the latter will tie us to a ring of

definite radius. It may be, however, that these conditions cannot both be satisfied, but there may still be—at different angles of incidence—a *dark* ring where the intensity I is a minimum. For a given angle of incidence R_2 , θ_2 and θ_1 are fixed, so that to find the dark ring we have to differentiate I with respect to Q .

In this way we learn that I is stationary when $Q = 1/R_2$. This makes $|q^2 r_2 r_3| = 1$ (see p. 517), so that the fundamental series cease to converge; but although we cannot thus go to the limit when $Q = 1/R_2$, we can make Q as near this as we please. The corresponding value of I is a *minimum* if $\cos(\theta_1 - \theta_2) - \cos(\theta_1 + \theta_2)$ is negative, which is always the case since I cannot be greater than unity.

The minimum value of I is $\frac{1 + \cos(\theta_1 - \theta_2)}{1 + \cos(\theta_1 + \theta_2)}$. The accompanying figure 14, drawn from the tables on pp. 535—536, will show how $\theta_1 - \theta_2$ varies in the neighbourhood of the polarising angle.

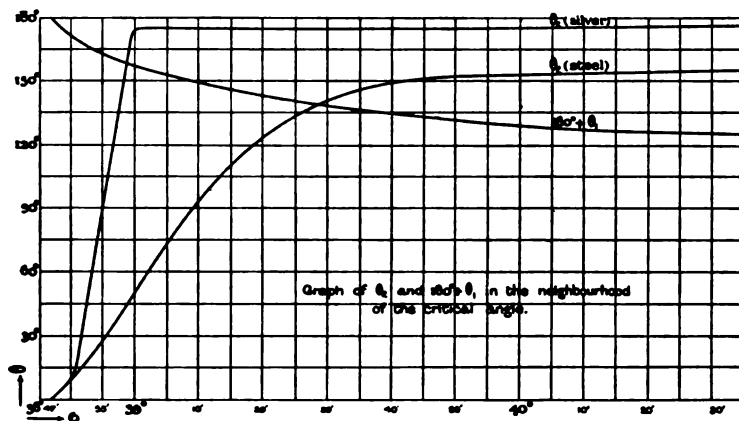


FIG. 14.

It will be at once obvious, on looking at the figure, that the variation of I is very much more rapid in the case of silver than of steel. With silver the rise of θ_2 from zero to 180° takes place almost entirely between the critical angle and 39° , i.e., within a space of only $13'$. As we have seen, there is absolute blackness when $\theta_2 - \theta_1 = 180^\circ$. This occurs with silver when $\phi = 38^\circ 59'$, and with steel when $\phi = 39^\circ 29'$.

The radius of the dark ring is obtained from the formula

$$R_2 = \frac{1}{Q} = \frac{1}{Q^2} = e^{2\pi\kappa/\lambda \cdot r^2 \sqrt{\sin^2 \phi - 1/\mu_1^2}},$$

which gives

$$\rho = r \sqrt{\frac{\kappa}{\lambda}} = \sqrt{\frac{\log_e R_2^2}{4\pi \sqrt{\sin^2 \phi - 1/\mu_1^2}}}.$$

From this we get the following values for the radii of the rings:—

Silver.

ϕ .	$38^\circ 47'$.	$38^\circ 50'$.	$38^\circ 55'$.	$38^\circ 59'$.	39° .
ρ	2.68	2.80	3.16	2.86	2.23

ϕ .	40° .	45° .	50° .	60° .	70° .	80° .
ρ	0.861	0.391	0.304	0.238	0.211	0.199

Steel.

ϕ .	$38^\circ 47'$.	39° .	$39^\circ 9'$.	$39^\circ 29'$.	40° .
ρ	1.95	2.01	1.88	1.46	1.09

ϕ .	45° .	50° .	60° .	70° .	80° .
ρ	0.465	0.342	0.245	0.206	0.186

Fig. 15 embodies these results, and shows in a graphic way how the ring expands and contracts as the angle of incidence increases.

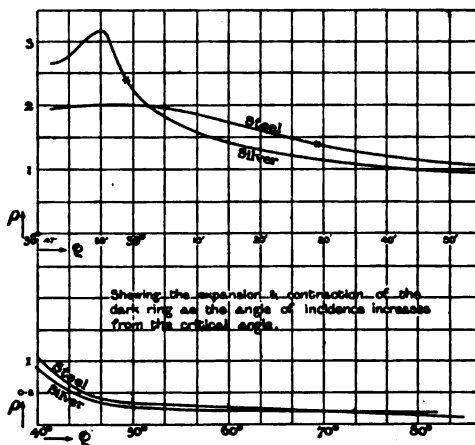


FIG. 15.

In order to show the variation clearly, it is necessary to represent ϕ on a different scale between the critical angle and 40° from what is employed beyond that. The crosses \times in the figure indicate the positions of the absolutely black ring. It will be observed that with silver the ring contracts very rapidly after the black ring has been reached, and that the contraction is not nearly so marked in the case of steel. In both cases the contraction after $\phi = 45^\circ$ is very slow.

The colour effects will be similar to those discussed earlier (*cf.* p. 524). For the black ring the value of ρ obtained above is 2.36 in the case of silver and 1.46 with steel. If, as before, we take these to correspond to the line D_1 in the spectrum, then for the lines A (red) and H (violet) we shall have $\rho_a = 2.68$, $\rho_h = 1.92$ for silver, and $\rho_a = 1.66$, $\rho_h = 1.19$ for steel.

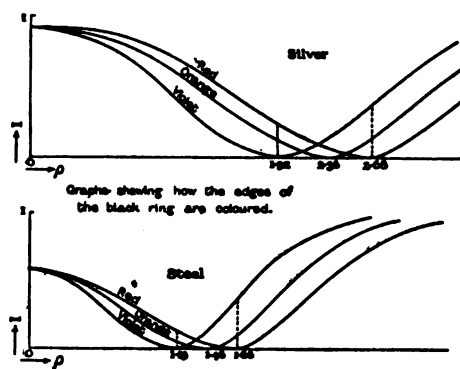


FIG. 16.

We have merely to plot the intensity for different colours, as is done in fig. 16 above, to see that the black ring is coloured red on the inside and violet on the outside. The intensity of the violet on the outside is greater than that of the red on the inside, so that the outside colour is more marked, as Stokes pointed out.

The minimum value of I is $\frac{1 + \cos(\theta_1 - \theta_2)}{1 + \cos(\theta_1 + \theta_2)}$. Its value very near the centre

is found by putting $Q = 1$, and so getting

$$I = \frac{1 + R_2^2 + 2R_2 \cos(\theta_1 - \theta_2)}{1 + R_2^2 + 2R_2 \cos(\theta_1 + \theta_2)}.$$

The value of I at the centre is given on p. 522. From the above formula for I we obtain the following results:—

Silver.

ϕ .	I (min.).	I (near centre).
38 47	1.000	1.000
38 50	0.971	0.980
38 55	0.531	0.974
39 0	0.384	0.972
40 0	0.789	0.834
45 0	0.948	0.950
50 0	0.972	0.972
60 0	0.986	0.986
70 0	0.993	0.993
80 0	0.997	0.997

Steel.

ϕ .	I (min.).	I (near centre).
38 47	1.000	1.000
39 0	0.681	0.819
39 9	0.344	0.722
40 0	0.019	0.506
45 0	0.759	0.776
50 0	0.876	0.880
60 0	0.949	0.950
70 0	0.975	0.975
80 0	0.989	0.989

If we wish to compare the phenomena in the case of reflection from metals with that from glass, we have (see p. 525) merely to put

$$r_2 = -r_1 = -e^{i\theta_1} = e^{i(\pi+\theta_1)},$$

which gives $R_2 = 1$ and $\theta_2 = \pi + \theta_1$. We thus get

$$I = \frac{(1-Q)^2}{(1-Q)^2 + 4Q \sin^2 \theta_1}$$

In this case there are no rings, but there is a dark spot at the centre. The spot is absolutely black at the point of contact where $Q = 1$. The intensity of its blackness diminishes rapidly as we proceed outwards, as is illustrated in figs. 17, 18, and 19 below. In these figures the ordinates represent the blackness $B = 1 - I$ for different angles of incidence.

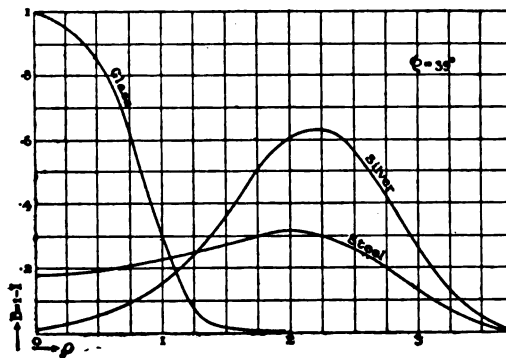


FIG. 17.

Fig. 17 represents the state of affairs when $\phi = 39^\circ$, i.e., within $13'$ of the critical angle. Here there is a very distinct dark ring. The ring is much more marked with silver than with steel, partly because the intensity of its

blackness is twice that with steel, and partly because the darkness near the centre is much smaller with silver than with steel, so that the contrast between the ring and its centre is increased.

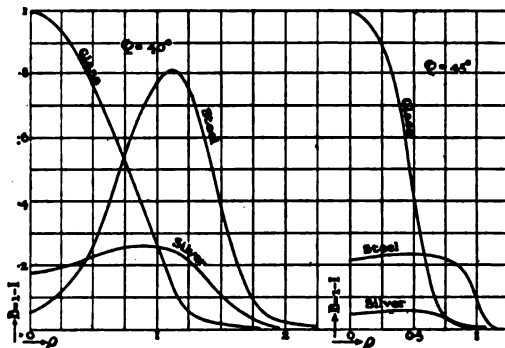


FIG. 18.

FIG. 19.

Fig. 18 illustrates the appearance when ϕ has increased to 40° . The dark ring with steel has now become very much more marked than formerly. Its intensity has increased, while the blackness at its centre has diminished. The ring with silver has contracted so much as to squeeze out its bright centre almost completely, so that it now presents the appearance of a dark spot at the centre, larger than with glass, but not so intense.

When ϕ has increased to 45° (fig. 19) the dark ring with steel has squeezed out the bright centre, and produced a dark central spot larger than with glass. The central spot with silver has become so faint as to be scarcely appreciable.

A glance at the tables on p. 540 will show that when ϕ is 50° or greater the maximum intensity of B is practically the same as that at the centre. There will thus be no ring, but a central dark spot, so faint, however, as to be barely visible.

Light polarised parallel to the Plane of Incidence.

In this case it is convenient to introduce a new vector (ξ', η', ζ') , of which (ξ, η, ζ) is the curl. Then we have

$$\xi' = 0 = \eta', \quad \xi = \frac{\partial \zeta'}{\partial y}, \quad \eta = -\frac{\partial \zeta'}{\partial x}, \quad \zeta = 0;$$

$$f = 0, \quad g = 0, \quad h = \frac{1}{\mu^2} \nabla^2 \zeta'.$$

To determine R_1 and θ_1 we must consider the passage of vibrations from glass to air.

In the glass

$$\zeta' = e^{ip[(x \cos \phi + y \sin \phi)/V - t]} \text{ (incident)} \\ + r_1 e^{ip[(-x \cos \phi + y \sin \phi)/V - t]} \text{ (reflected).}$$

In the air

$$\zeta' = s_1 e^{ip[(nx + y \sin \phi)/V - t]} \text{ (refracted),}$$

where n has the same value as on p. 533.

The boundary conditions give

$$1 + r_1 = s_1 \quad \text{and} \quad 1 - r_1 = n/\cos \phi \cdot s_1,$$

whence

$$r_1 = e^{i\theta_1} \quad \text{where} \quad \tan \frac{1}{2}\theta_1 = -\frac{\sqrt{\sin^2 \phi - 1/\mu_1^2}}{\cos \phi}.$$

Similarly, R_2 and θ_2 will be determined by considering the passage of vibrations from air to metal.

In the air

$$\zeta' = e^{ip[(nx + y \sin \phi)/V - t]} \text{ (incident)} \\ + r_2 e^{ip[(-nx + y \sin \phi)/V - t]} \text{ (reflected).}$$

In the metal

$$\zeta' = (\mu/\mu_0)s_2 e^{ip[(mx + y \sin \phi)/V - t]} \text{ (refracted),}$$

where m has the same value as on p. 535.

The boundary conditions give

$$1 + r_2 = \frac{\mu^2}{\mu_0^2} s_2 \quad \text{and} \quad 1 - r_2 = \frac{m}{n} \frac{\mu^2}{\mu_0^2} s_2,$$

whence

$$r_2 = \frac{1 - m/n}{1 + m/n}.$$

In the case of a metal like silver m/n is real and equal to γ , so that we get

$$R_2 e^{i\theta_2} = r_2 = -\frac{\gamma - 1}{\gamma + 1},$$

so that

$$R_2 = \frac{\gamma - 1}{\gamma + 1} \quad \text{and} \quad \theta_2 = \pi.$$

Since $\theta_2 = \pi$, it follows that $\cos(\theta_1 - \theta_2) = \cos(\theta_1 + \theta_2)$ so that the numerator and denominator in the expression for I are the same. Thus $I = 1$ everywhere, and there are no rings. The only point where there is any darkness is where the glass and metal are in contact. The intensity in this case is given on p. 530. There will thus be a small dark spot at the centre, much smaller than in the case of glass.

For metals, like steel, for which m/n is not real, we have

$$m/n = -i\gamma' \quad \text{and} \quad r_2 = \frac{1 + i\gamma'}{1 - i\gamma'};$$

whence

$$R_2 = 1 \quad \text{and} \quad \tan \frac{1}{2}\theta_2 = \gamma'.$$

Putting $R_1 = R_2 = 1$ in the formula for I we get

$$I = \frac{1 + Q^2 + 2Q \cos(\theta_2 - \theta_1)}{1 + Q^2 + 2Q \cos(\theta_2 + \theta_1)}.$$

This is a minimum when $Q = 1$, i.e., at the centre, and its value there is $\frac{1 + \cos(\theta_2 - \theta_1)}{1 + \cos(\theta_2 + \theta_1)}$. There will be absolute blackness at the centre when $\theta_2 - \theta_1 = \pi$.

The following table gives the values of θ_1 , θ_2 and the minimum intensity for different values of ϕ :—

Steel

ϕ .	$-\theta_1$.	θ_2 .	I (min.).
$38^\circ 47'$	$0^\circ 0'$	$180^\circ 0'$	0.000
$39^\circ 0'$	$8^\circ 58'$	$174^\circ 58'$	0.077
$40^\circ 0'$	$21^\circ 20'$	$167^\circ 58'$	0.080
$45^\circ 0'$	$49^\circ 48'$	$152^\circ 24'$	0.095
$50^\circ 0'$	$68^\circ 52'$	$142^\circ 34'$	0.115
$60^\circ 0'$	$100^\circ 12'$	$128^\circ 24'$	0.180
$70^\circ 0'$	$127^\circ 56'$	$118^\circ 40'$	0.303
$80^\circ 0'$	$154^\circ 16'$	$112^\circ 48'$	0.568

With glass we have

$$I = \frac{(1 - Q)^2}{(1 - Q)^2 + 4Q \sin^2 \theta_1},$$

so that there is absolute blackness at the centre. The following table enables us to compare the intensity with glass and steel at different distances from the centre :—

ρ .	0.	0.5.	1.	2.
$\phi = 40^\circ$ {				
Q	1.000	0.597	0.127	0.00026
I (steel)	0.080	0.494	0.952	0.9997
I (glass) ...	0.000	0.339	0.919	0.9997
$\phi = 60^\circ$ {				
Q	1.000	0.391	0.023	$10^{-7} \times 3$
I (steel)	0.180	0.345	0.981	1.000
I (glass)	0.000	0.197	0.914	1.000

These results are represented graphically in fig. 20, from which it appears that there is little difference between the phenomena with steel and glass.

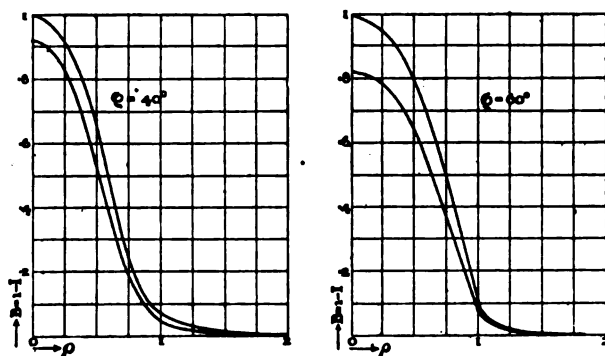


FIG. 20.

It would seem, then, that all the remarkable phenomena of Newton's rings formed by metallic reflection, to which Stokes drew attention, are in accordance with the known principles of metallic reflection, without requiring the introduction of effects of gradual transition between the media.

On the Laws of Radiation.

By J. H. JEANS, M.A., Fellow of Trinity College, Cambridge, Professor of
Applied Mathematics in the University of Princeton.

(Communicated by Professor J. Larmor, Sec. R.S. Received October 11,—
Read November 16, 1905.)

1. An attempt to obtain the law of partition of the radiation proceeding from a radiating body calls at the outset for a consideration of the partition of energy between the matter of which the radiating body is composed, and the ether by which it is surrounded. This question has been discussed by Lord Rayleigh* and by the present author.† Assuming that the ultimate state of equilibrium between the energies of matter and ether has been reached, the theorem of equipartition of energy enables us to determine the amount not only of the total energy of the ether, but also of the energy of each wave-length. It is found that at a temperature T , the energy per unit volume of radiation consisting of waves of wave-lengths between λ and $\lambda + d\lambda$ is

$$8\pi RT\lambda^{-4}d\lambda.$$

It is obvious that this law, according to which the energy tends to run entirely into waves of infinitesimal wave-length, cannot be the true law of partition of the radiant energy which actually occurs in nature. The law is obtained from the supposition that a state of statistical equilibrium has been arrived at between the energies of different wave-lengths and that of matter; the inference to be drawn from the failure of this law to represent natural radiation is that in natural radiation such a state of equilibrium does not obtain. An analogous situation presents itself in the theory of gases. According to the theorem of equipartition of energy, the energy of a gas will ultimately be almost entirely absorbed by the modes of internal vibration of its molecules, whereas it is known that in nature only a very small fraction of the energy is possessed by these internal vibrations. Thus we are led to suppose that there is not a state of equilibrium between the internal vibrations of the molecules and their energy of translation; we find that the transfer of energy from the translational to the vibrational degrees of freedom is so slow that the latter degrees never acquire their full share of energy, as given by the theorem

* "On the Dynamical Theory of Gases and Radiation," 'Nature,' May 18, July 13, 1905.

† "On the Partition of Energy between Matter and Ether," 'Phil. Mag.' [6], vol. 10, p. 97.

of equipartition, the energy of these vibrations being dissipated away as rapidly as it is received from the translational energy of the molecules. A similar explanation suggests itself in the case of the partition of radiant energy. In the present paper an attempt is made to show that such an explanation is in accordance with the observed facts. The radiant energy acquired by the ether, whether of small or of great wave-length, is reabsorbed by other bodies or is radiated away into space, in such a way that the partition of the energy actually present in the ether at any instant is entirely different from that predicted by the law of equipartition.

On this view, the true laws of radiation can be obtained only through a study of the processes of transfer of energy from matter to ether. This in turn demands the use of hypotheses or assumptions as to the structure of matter and the mechanism by which radiation is produced. The view of the genesis of radiation which will be taken in the present paper is one which has already been put forward and developed to a considerable extent by Lorentz.*

2. The radiation from all solid bodies shows the same general characteristics, and according to this view, the common basis of these characteristics is the presence of free electrons in the source of radiation. As the electrons describe curved paths, they yield up energy to the ether, and the part of this energy which escapes reabsorption by matter figures as the energy of radiation represented in the continuous spectrum of a solid.

In addition to free electrons, there will also be present in the radiator a number of atoms, these also being charged with electricity. The atoms and complete molecules of the solid must be supposed to be so closely packed that there is not room for them to move past one another. Thus these bodies merely oscillate about their positions of equilibrium, while the electrons thread their way through the interstices. No matter what forces are at work between the electrons and the larger masses, or how closely the latter are packed, the law of distribution of velocities of the molecules, of the atoms, and of the electrons, will be Maxwell's law.† From this law, it follows that the velocities of the atoms and molecules will, on account of their greater mass, be very much smaller on the average than the velocities of the free electrons. Thus the atoms or molecules may, with considerable closeness of approximation, be regarded simply as fixed obstacles, against which the electrons impinge. The emitted radiation being regarded as the result solely of the motion of electric charges, it follows that the slow motion of complete

* "On the Emission and Absorption by Metals of Rays of Great Wave-length," Akad. van Wetenschappen, Amsterdam, April 24, 1903.

† Cf. the author's "Dynamical Theory of Gases," § 86.

atoms or molecules will contribute but little to the total radiation, this radiation proceeding almost entirely from the more rapid motions of the free electrons as they thread their way through the solid.

As the electrons move, that part of their energy which is yielded up to the ether, assumes the form of radiant energy, and travels through the ether in all directions with a uniform velocity V , the velocity of light, except in so far as this radiant energy is obstructed or reabsorbed by matter. Let us suppose the boundary of the radiator to be a semi-infinite plane. Then if κ is a coefficient of extinction, the energy generated at a point distant r from some specified small area on the boundary, will, by the time it crosses the boundary through this small area, be reduced in the ratio $e^{-\kappa r}$. Supposing energy to be yielded up to the ether at a uniform rate G per unit volume per unit time throughout the radiator, the stream of energy crossing unit area of the boundary

$$= \int_0^{\infty} \frac{G}{4\pi r^2} e^{-\kappa r} \pi r^2 dr = \frac{G}{4\kappa},$$

a definite finite quantity. The contribution to the total stream of radiation from large values of r is infinitesimal, so that we may regard the stream of energy which crosses the boundary at any point as proceeding only from those parts of the radiator which are in the immediate neighbourhood of the point. Thus the shape and size of the radiator do not influence the stream of radiation issuing from a point on its surface; it is only the structure of the surface-layers at the point which is of importance.

3. Let us suppose that at any point of the surface the energy of the issuing radiation, of which the wave-length lies between λ and $\lambda + d\lambda$ is

$$\phi(\lambda, T) d\lambda \quad (i)$$

per unit volume, T being the temperature of the radiator. Our problem is to discuss the form of the function ϕ .

In addition to depending on λ and T , the function ϕ will involve the following quantities:—

V , the velocity of light;

e , the charge of an electron;

m , the mass of an electron;

R , the constant of the theory of gases, this being such that the mean kinetic energy of an electron is $\frac{3}{2}RT$;

K , the inductive capacity of the ether, measured in whatever units are in use;

k_1, k_2, k_3, \dots , quantities specifying the structure of the radiating solid, *e.g.*, the number of free electrons per unit volume, the shape, size, mass, etc., of the atoms and molecules.

Thus the law of radiation can be expressed more completely by

$$\phi(\lambda, T, V, e, m, R, K, k_1, k_2, \dots) d\lambda. \quad (\text{ii})$$

By solving the equations

$$\frac{\partial}{\partial k_1} \int \phi d\lambda = 0, \quad \frac{\partial}{\partial k_2} \int \phi d\lambda = 0, \text{ etc.}, \quad (\text{iii})$$

we obtain the values of k_1, k_2, \dots for which the function $\int \phi d\lambda$ possesses its maximum value. We therefore obtain a knowledge of the properties of the solid body, which is such that the total radiation at a given temperature is a maximum. Let us refer to this body as the "radiator of maximum efficiency" for the temperature in question, and let us denote the value of ϕ for this "radiator of maximum efficiency" by ϕ_m . If we eliminate k_1, k_2, \dots from equations (ii) and (iii) we obtain ϕ_m as a function of

$$\lambda, T, V, e, m, R, \text{ and } K. \quad (\text{iv})$$

4. In terms of the units, L of length, M of mass, t of time, K of inductive capacity, and T of degrees of temperature, the physical dimensions of these seven quantities are as follows:—

λ is of dimensions.....	L
T	T
V	Lt^{-1}
e	$L^{\frac{1}{2}}M^{\frac{1}{2}}t^{-1}K^{\frac{1}{2}}$
m	M
R	$LMt^{-2}T^{-1}$
K	K

Here are seven quantities and five independent physical units. It must, therefore, be possible to combine the seven quantities in two independent ways so as to form a mere number. We may take as two independent expressions formed from these seven quantities, so as to have the dimensions of a number,

$$c_1 \equiv RTm^{-1}V^{-2}, \quad c_2 \equiv \lambda RTKe^{-2}.$$

Any other pure number which can be formed from these seven quantities must be of the form $f(c_1, c_2)$.

The physical dimensions of the function ϕ_m are those of energy per unit volume per unit wave-length, hence ϕ_m is of dimensions $L^{-3}Mt^{-2}$. These dimensions are those of $\lambda^{-4}RT$. The ratio of ϕ_m to this quantity is, therefore, a pure number, and from this it follows that it must be possible to express ϕ_m in the form

$$\phi_m = \lambda^{-4}RTf(c_1, c_2). \quad (\text{v})$$

5. There is an obvious physical interpretation of the number c_1 . The mean kinetic energy of a free electron at temperature T is $\frac{3}{2}RT$, so that the value of C^2 , the mean square of its velocity, is $\frac{3}{2}RTm^{-1}$. Thus $\frac{3}{2}c_1$ is equal to C^2/V^2 . At a temperature of 100°C ., the value of C is 7×10^6 cm. per second,* while the value of V is 3×10^{10} . The value of c_1 is accordingly 3.6×10^{-8} , a quantity sufficiently small to be neglected. On passing to the limit in which c_1 is put equal to zero, the function $f(c_1, c_2)$ either may or may not tend to a definite limit $f(0, c_2)$. For the present we shall assume such a limit to exist, without entering upon a discussion of the exact meaning of this assumption.

6. On this assumption, since the actual value of c_1 is very small, we find that ϕ_m may very approximately be expressed in the form

$$\phi_m = \lambda^{-4}RTf(c_2);$$

or, replacing c_2 by its value and dropping the universal constants R , T , K and e ,

$$\phi_m = \lambda^{-4}Tf(\lambda T).$$

Thus the law of radiation from the radiator of maximum efficiency for temperature T and wave-length λ is

$$\lambda^{-4}Tf(\lambda T)d\lambda.$$

7. The radiator of maximum efficiency has been defined so as to have reference to a given temperature. It is a purely ideal body, and there is no evidence given as yet whether or not its properties can be obtained even approximately from actual matter. The values of k_1, k_2, \dots given by equations (iii) are functions of T , so that even if a natural body approximates closely to the radiator of maximum efficiency at a given temperature, it cannot be expected to do so at all temperatures. At the same time it is possible for us to imagine a purely ideal radiator which shall possess the property of being the radiator of maximum efficiency at all temperatures, the properties of this body changing in such a way that equations (iii) are satisfied at all temperatures. Let us agree for the present to speak of such a body as a "perfect radiator."

8. The law of radiation for a perfect radiator has been seen to be

$$\lambda^{-4}Tf(\lambda T)d\lambda. \quad (\text{vi})$$

On integrating with respect to λ , we obtain at once that the total radiation is of the form σT^4 , where $\sigma = \int_0^\infty x^{-4}f(x)dx$. This is the expression of Stefan's law. Let the wave-length at which the energy per unit wave-

length, *i.e.*, the coefficient of $d\lambda$ in expression (vi), is a maximum, be denoted by λ_{\max} ; then we find at once that $\lambda_{\max}T$ is a root of

$$\frac{\partial}{\partial x} \{x^{-4}f(x)\} = 0,$$

so that we have the relation

$$\lambda_{\max}T = a, \quad (\text{vii})$$

where a is a constant. This is the mathematical expression of Wien's displacement-law. Thus we see that the two laws, which are usually obtained by thermodynamical arguments, can be obtained simply by an argument from physical dimensions, coupled with the hypothesis that the source of radiation is the motion of electrical charges.

9. The argument from physical dimensions can, however, be used in a second way: we can obtain by its help a rough numerical estimate of some of the quantities concerned. For instance the constant σ of Stefan's law is a function only of V , e , m , R and K , and is of dimensions $L^{-2}Mt^{-2}T^{-4}$. Now the only way in which the quantities V , e , m , R , and K can be combined so as to form a quantity of the dimensions of σ is through an expression of the form $e^{-6}R^4K^3$. Hence, by using an argument which I have explained in another place,* it can be shown that σ must be equal, as regards order of magnitude, to $e^{-6}R^4K^3$.

Similarly it can be shown that the constant a of Wien's law must be equal, as regards order of magnitude, to $e^2R^{-1}K^{-1}$.

The values of σ and a have been obtained experimentally.† In C.G.S. centigrade units, the value of σ obtained from Kurlbaum's experiments is 5.32×10^{-5} , while the value of a obtained by Lummer and Pringsheim is 0.294. Let us use these values in conjunction with the approximate theoretical values already obtained, to deduce the value of e , the charge on the particles by which radiation is generated. On taking the value‡ $R = 9.3 \times 10^{-17}$ we find from the approximate equality

$$e^{-6}R^4K^3 = 5.32 \times 10^{-5},$$

the value

$$eK^{-\frac{1}{3}} = 1.8 \times 10^{-10},$$

while from the second relation,

$$e^2R^{-1}K^{-1} = 0.294,$$

* "On the Vibrations and Stability of a Gravitating Planet," 'Phil. Trans.,' A, vol. 201, p. 158.

† An account of experimental determinations of these constants is given by Lummer, 'Congrès de Physique, Paris (1901) Rapports,' vol. 2, pp. 92–96.

‡ Cf. the author's 'Dynamical Theory of Gases,' p. 113.

we obtain $eK^{-\frac{1}{2}} = 51 \times 10^{-10}$. The value of $eK^{-\frac{1}{2}}$ obtained experimentally,* is 3×10^{-10} . The difference between this and the values obtained above is not greater than may fairly be ascribed to the roughness of the method used. For example, the calculations would have been the same if e had been measured in "rational" electric units instead of those in common use, but we should then have had an experimental value equal to 4π times that mentioned above, say $eK^{-\frac{1}{2}} = 38 \times 10^{-10}$. The comparative agreement between the theoretically predicted value and the true value must, therefore, be regarded as evidence that we are on the right track in attempting to obtain the laws of radiation from the supposition that the radiation proceeds from the motion of electrons.

10. On this supposition, the law of radiation for waves of great wave-length has been determined by Lorentz. His analysis rests upon the assumption, which we have already made, that the velocity of the electrons is small compared with that of light, and he makes the further assumption that the motion of the electrons may be regarded as a series of free paths separated by instantaneous collisions. On these assumptions, he obtains as the emission from a radiator

$$8\pi A R T \lambda^{-4} d\lambda, \quad (\text{viii})$$

where A is the coefficient of absorption, as determined by Drude's theory.† The second assumption, that of undisturbed free paths and instantaneous collisions, although doubtless reproducing in the main the essential physical properties of the motion, will not necessarily lead to results which are numerically exact. It may be found that the results obtained require to be modified by the introduction of a numerical multiplier, just as Clausius' formula for the mean free path in a gas requires to be multiplied by a numerical factor to allow for the varying velocities of the individual molecules. We may, however, infer from Lorentz's analysis that the radiation, for great values of λ , is accurately proportional to $T \lambda^{-4} d\lambda$.

We can also obtain some idea of the form assumed by the law of radiation when λ is very small. The rate at which radiation of short wave-length λ is produced by collisions of electrons will contain as its most important feature a factor of the form e^{-n} , where n is a large number, comparable with the ratio of the average duration of a collision to the period of vibration λ/V .‡ Thus the radiation when λ is very small will vanish in the same way as the exponential $e^{-\tau V/\lambda}$ where τ is comparable with the duration of a collision.

* J. J. Thomson, 'Phil. Mag.' [6], vol. 5, p. 335.

† Drude's 'Annalen,' vol. 1, p. 576.

‡ Cf. "On the Application of Statistical Mechanics to the General Dynamics of Matter and Ether," 'Roy. Soc. Proc.," vol. 76, p. 296, § 13.

On comparison with the form of the general law of radiation, as given by expression (vi), it is seen that this factor must be of the form $e^{-c/\lambda T}$, and it is worthy of notice that every empirical law of radiation reduces when λ is very small to a form in which a factor of this type is the factor of preponderating importance.

11. To summarise the information which has been obtained, we may say that :—

(1) The law of radiation from a perfect radiator is of the form

$$\lambda^{-4} T f(\lambda T) d\lambda,$$

so that Stefan's law and Wien's displacement law are accurately obeyed by the radiation from this ideal radiator.

(2) For large values of λT , the form of the function $f(\lambda T)$ approximates to a constant, a result due to Lorentz.

(3) For small values of λT , the form of the function $f(\lambda T)$ is such that it decreases very rapidly as λ decreases, finally vanishing in the same way as the function $e^{-c/\lambda T}$.

A discussion of the relation between the radiation from our ideal "perfect radiator" and that from actual bodies, may appropriately be reserved for a later paper.

The Transit of Ions in the Electric Arc.

By A. A. CAMPBELL SWINTON.

(Communicated by the Hon. C. A. Parsons, C.B., F.R.S. Received October 24,—
Read November 16, 1905.)

According to the most modern view, as enunciated by Professor J. J. Thomson in one of his recent works,* the phenomenon known as the Electric Arc is explained on the assumption that the positive and negative electrodes emit respectively positively and negatively electrified corpuscles or ions, which, under the influence of electric repulsion, travel across the space occupied by the arc and bombard the electrode opposite to the one from which they have been emitted. It is further supposed that the electric current is itself conveyed by these ions, and that the high temperature of the electrodes is produced by their bombardment.

About a year ago it occurred to the writer that it should be possible to test the correctness of, at any rate, some portion of this theory by deflecting—by means of a magnet—either the positive or the negative ions into a Faraday cylinder placed with its aperture just touching the centre of the arc, in a manner somewhat similar to that adopted by Perrin,† for demonstrating the electric charge carried by cathode rays. The experiment was tried, but it was found that no definite results could be obtained, owing to the erratic behaviour of the arc, which proved very unmanageable, and preferred to divide itself into two arcs between the carbon electrodes and the exterior of the Faraday cylinder, which was rapidly destroyed by fusion.

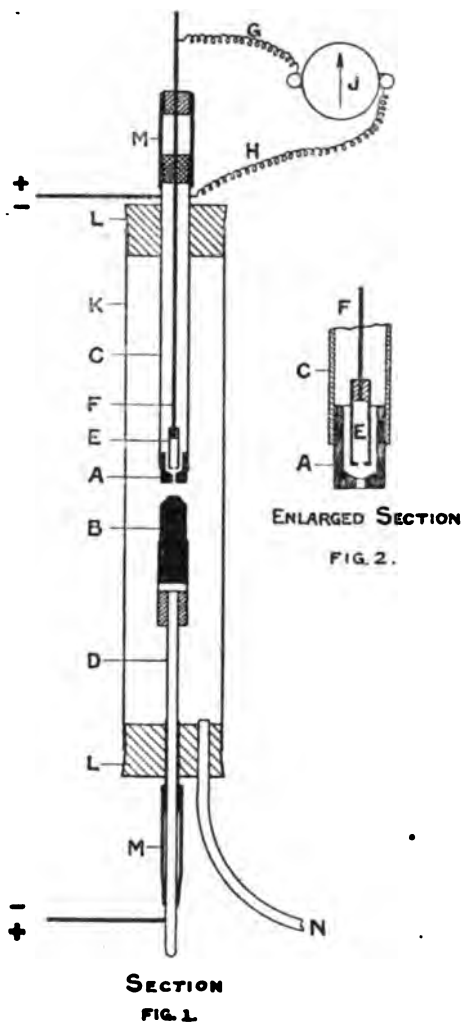
More recently the writer has made the experiment again in a somewhat modified form, and has obtained results which appear to prove conclusively that the theory, as above described, is correct, and that positively and negatively charged carriers do actually travel from the positive and negative electrodes respectively along the arc in opposite directions, and do bombard the opposite electrodes.

The apparatus is shown in section in fig. 1, in which "A" and "B" are two electrodes of ordinary arc-lamp carbon. The upper electrode, "A," is fixed rigidly in one end of the fixed brass tube, "C," while the lower electrode, "B," is held in a similar tube having a sliding arrangement at "D," whereby it can be slightly moved so as to bring the carbons into contact for the purpose of striking the arc.

* 'Conduction of Electricity through Gases,' 1903.

† 'Comptes Rendus,' vol. 121, p. 1130, 1895.

A small hole is pierced axially through the upper electrode, and immediately behind this aperture is fixed the insulated Faraday cylinder, "E," which has its aperture in line with, and facing, the aperture in the electrode. By means of an insulated brass rod, "F," and the conductors,



"G" and "H," any difference of potential between the Faraday cylinder and the upper electrode—which, with the brass tube, "C," completely encloses the cylinder—can be measured by means of the mirror galvanometer, "J." Fig. 2 shows an enlarged section of the Faraday cylinder and the pierced electrode.

Current for the experiments was obtained from the 200-volt continuous-current public supply, resistances being inserted in the circuit so as to keep the current down to about 3 ampères with some 50 volts across the arc.

The first experiments were made with the apparatus in air at ordinary atmospheric pressure. Under these conditions no results were obtained. Having regard to the small velocity that the ions could have under the comparatively small potential difference across the arc, the considerable distance the ions would have to travel in order to enter the Faraday cylinder, and the density of the air at ordinary atmospheric pressure, this was to be expected.*

The apparatus was next enclosed in the glass tube, "K," with rubber stoppers, "L," at the ends, the moving parts being rendered air-tight by the rubber tubes, "M." By means of the tube, "N," the whole was connected to a mechanical air-pump capable of giving moderate degrees of vacuum.

With a very small degree of exhaustion—about half an atmosphere—it was found that if "A" were made the positive and "B" the negative electrode, immediately the arc was started a positive electric current, passing from "A" to the Faraday cylinder, and showing that the latter had become negatively charged, was indicated by the galvanometer.

As the exhaustion proceeded, this current was found to increase, and at a still moderate degree of exhaustion, on reversing the current in the arc, and making "A" negative and "B" positive, it was found that the positive current, through the galvanometer, passed from the Faraday cylinder to "A," showing that the cylinder was positively charged.

In each case these results were obtained with degrees of exhaustion at which the arc still retained its normal characteristics, while the fact that the effects were only produced when the arc played on the upper electrode so as to cover the aperture, no deflection of the galvanometer taking place when the arc was deflected by means of a magnet, so as not to cover the aperture, showed very clearly that the electrification of the Faraday cylinder was due to ions passing from the arc through the aperture. This was also proved by plugging the aperture in the electrode with a small piece of carbon. When so plugged, no deflection of the galvanometer could be obtained.

Whether the electrode "B" were made positive or negative, it was found that the galvanometer deflections increased considerably with the degree of exhaustion, while, at any given degree of exhaustion, a considerably

* Since this paper was communicated the writer has succeeded, by employing larger arcs of from 10 to 12 ampères, and by slightly enlarging the aperture in the upper electrode, to obtain all the results described in air at ordinary atmospheric pressure.

larger deflection was obtained when "B" was made negative than when it was made positive. These results correspond with the known fact that negative ions have a greater velocity than positive ions.

As was to be expected, having regard to the unstable nature of the arc, the galvanometer deflections were not very steady. They were, however, invariably in the directions indicated, according as the polarity of the electrodes was transposed, and endured as long as the arc covered the aperture in the upper electrode.

The writer is indebted to Mr. J. C. M. Stanton and Mr. R. C. Pierce for their skilful assistance in carrying out the above experiments.

The Accurate Measurement of Ionic Velocities.

By R. B. DENISON, M.Sc., Ph.D., and B. D. STEELE, D.Sc.

(Communicated by Sir William Ramsay, K.C.B., F.R.S. Received October 14,—
Read November 16, 1905.)

(Abstract.)

The value of the direct method of measuring ionic velocities has been seriously diminished in the past by the necessity of using gelatine solutions in the measuring apparatus, and by the restriction of the method to more concentrated solutions.

The authors have succeeded in devising an apparatus in which it is possible to compare and measure the velocities of the ions of a given salt without using gelatine or other partitions during the actual experiment; and they have also succeeded in extending the method to the measurement of dilute solutions.

The apparatus consists of two reservoirs, each supplied with a special electrode vessel, and of a measuring-tube of known cross-section, in which the solution to be measured is placed. One of the reservoirs contains a solution of a salt which has a slower cation than that to be measured, and the other a solution of a salt with a slower anion than that to be measured. When a current is passed in the proper direction through such a system, an electrolytic margin of constant velocity is formed, provided certain conditions are fulfilled. These conditions have been already described.* The measuring tube is provided at each end with a parchment-paper partition, which facilitates the formation of a sharp electrolytic margin between the indicator

* Masson, 'Phil. Trans.,' A, 1899, p. 331; Steele, A, 1902, p. 105.

and measured solutions, and these partitions are so arranged that they can be removed from the ends of the measuring-tube after the margins have been formed. There is thus no membrane of any sort between the two electrodes, and electrolysis is not complicated by the occurrence of electric endosmose.

The formation of bubbles of hydrogen or oxygen gas in the electrode vessels is prevented by the use of unpolarisable electrodes.

The transport number and the average absolute velocity of the ions of a number of salts have been measured with very satisfactory results. Transport numbers have been measured at dilutions down to one-fiftieth normal, and the following results will serve to illustrate the degree of accuracy obtained.

Salt.	Concentration.	Transport number.	
		Denison and Steele.	By Hittorf's method.
KCl	$n/10$	0.508	0.508
	$n/50$	0.507	0.507
NaCl	$n/10$	0.618	0.617
	$n/50$	0.614	0.613
HCl	$n/10$	0.165	0.172
KOH	$n/1$	0.738	0.735

The values which we have obtained for the average absolute velocities confirm in a remarkable manner those calculated from conductivity data by Kohlrausch. This will be seen from the following examples:—

$$T = 18^{\circ} \text{C.}$$

Salt and concentration.	Velocities in cm./sec.			
	Anion velocities.		Cation velocities.	
	Found. Denison and Steele.	Calculated. Kohlrausch.	Found. Denison and Steele.	Calculated. Kohlrausch.
KCl 0.1 % ...	0.000582	0.000588	0.000563	0.000568
NaCl 0.1 % ...	0.000591	0.000591	0.000367	0.000367
KClO ₃ 0.1 % ...	0.000474	0.000476	0.000549	0.000550
HCl 0.1 % ...	0.000600	0.000626	0.000303	0.000303

It is claimed for the present method that it is at least as accurate as that of Hittorf, and an experiment can be carried out in about one-tenth of the time. It also gives a means of comparing the degree of dissociation of salts containing a common ion.

The Physical and Chemical Properties of Iron Carbonyl.

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S., Jacksonian Professor in the University of Cambridge, and HUMPHREY OWEN JONES, M.A., D.Sc., Fellow of Clare College, and Jacksonian Demonstrator in the University of Cambridge.

(Received October 24,—Read November 16, 1905.)

This paper contains an account, as promised, of a study of the physical and chemical properties of iron carbonyl, similar to that already communicated to the Society on the properties of the analogous compound of nickel,* to which this forms the sequel.

The combination of iron and carbon monoxide was discovered by Drs. Mond and Quincke in 1891,† and the resulting compound called iron pentacarbonyl was isolated (as a coloured liquid), and examined by Drs. Mond and Langer‡ in the course of the same year.

Our knowledge of this remarkable substance is derived entirely from the observations of the last-named investigators, and a few isolated observations of others—thus the late Dr. Gladstone determined its refractive indices and Dr. Perkin the magnetic rotation. The molecular refractive power and magnetic rotation are abnormally high, and the compound is diamagnetic; such remarkable properties naturally aroused considerable interest, but the lack of any further work on the compound is doubtless due to the great difficulty experienced in preparing quantities of the compound large enough to work with.

The peculiarities exhibited by this compound call for further attention, and we have examined the formation of the compound and its properties, both physical and chemical; the investigation has been carried out on the same lines as that on nickel carbonyl,§ and attention has been directed more particularly to the differences between the iron and nickel carbonyls, such as the difference in formula, colour, stability and, more especially, to the action of light on iron carbonyl.

We are indebted to Dr. Mond for two specimens of iron carbonyl with which the investigation was begun; latterly we have been able to prepare and use much larger quantities of the compound, and further work is still

* 'Roy. Soc. Proc.,' 1903, vol. 71, p. 427.

† 'Trans. Chem. Soc.,' 1891, vol. 59, p. 604.

‡ 'Trans. Chem. Soc.,' 1891, vol. 59, p. 1090.

§ *Loc. cit.*, and 'Trans. Chem. Soc.,' 1904, vol. 85, p. 203, p. 213.

in progress. The preparation of iron carbonyl in quantity is a long and tedious process; the yield obtained depends on a number of circumstances; the best conditions for the preparation of the compound are being investigated, and it is hoped that the observations made on this subject will form the subject of another communication.

Liquid iron carbonyl is described as a yellow liquid, with the formula $\text{Fe}(\text{CO})_5$, boiling at $102^{\circ}\text{--}8^{\circ}\text{C}$. It is remarkable that nickel carbonyl, the compound of a metal whose salts are highly coloured, is colourless, while iron carbonyl is coloured, and the salts of iron have usually only a feeble colour. Also the difference in composition, coupled with the higher boiling point of the iron compound, caused by the introduction of more carbon monoxide, is a striking phenomenon. We considered it important to determine whether careful purification and drying of the compound would remove the colour, and to procure further analytical evidence bearing on its formula.

To purify the substance it was placed with some suitable drying agent (copper sulphate, barium oxide, zinc chloride, and pure phosphorous pentoxide were all found suitable) in one limb of a carefully-dried glass tube bent into the form of a V-tube; the other limb was empty. The tube was then exhausted by means of a side tube, filled several times with carbon monoxide, hydrogen or nitrogen, exhausted again, and then the side tube was sealed off. After standing in the dark for some time the iron carbonyl was distilled into the empty limb by placing this in a freezing mixture and the other limb in a beaker of water at about 50°C . The liquid was still of a pale yellow colour, even after standing several days over phosphorous pentoxide and distilling by feeble gas-light.

Another form of experiment showed conclusively that the colour is a definite property, and is not due to impurities. A tube bent into the form of an M was used, the liquid was allowed to stand in one limb for several days over anhydrous copper sulphate, distilled over into the bend, where it was allowed to stand for a week over pure phosphorous pentoxide, and then finally distilled into the empty limb of the tube. The operations were carried out in the dark, and the liquid still possessed its yellow colour. Consequently, it is concluded that the pure compound has a yellow colour. We have therefore not been able to confirm the opinion expressed by Armstrong* that the pure compound would be colourless.

For analysis the compound was purified as described above, and rapidly transferred to weighed glass bulbs in a vacuum desiccator, the bulbs sealed and weighed. The transference must be effected very rapidly, as the com-

* 'Proc. Chem. Soc.,' 1893, p. 58.

pound is exceedingly sensitive to air and moisture; a reddish precipitate is produced on standing if the liquid has been exposed even for a very short time to moist air.

The percentage of carbon monoxide was determined by combustion. It was found necessary, in order to get constant results, to pass a current of oxygen through the tube for a long time, while heated to a bright red heat, in order to completely oxidise the carbon which was deposited with the iron.

(1) 0.2680 gramme of the liquid gave 0.3000 gramme of carbon dioxide.

(2) 0.4336 " " 0.4825 " "

The estimation of the iron offered greater difficulties. Mond and Langer* decomposed the compound by heating to 100° C. with chlorine or bromine water in a sealed tube, and then weighing the iron as ferric oxide.

This method always gave slightly high results, and accuracy is limited because small quantities only can be used on account of the great pressure developed.

(3) 0.3417 gramme gave 0.1424 gramme of ferric oxide.

A bulb containing a weighed quantity of the liquid was broken under a chloroform solution of bromine, the gas evolved was passed through more of the same solution in a U-tube. When the reaction had ceased the solutions were evaporated to dryness, and the iron precipitated and weighed as ferric oxide.

(4) 0.7820 gramme gave 0.3209 gramme ferric oxide.

The best method of decomposing the compound was found to be treatment with alcoholic potash solution in a sealed tube at 100° C. When a bulb containing iron carbonyl was broken in alcoholic potash solution, beautiful colourless tabular crystals having a pearly lustre were at once produced; at the surface of the liquid these were at once oxidised by the air with the formation of a reddish brown precipitate.

The mixture contained in a sealed tube was heated to 100° C. for a short time, the tube cooled, opened (no pressure is produced by this decomposition), the contents washed out and evaporated to dryness. The residue was treated with nitric acid, again evaporated down, and the iron precipitated by hot caustic potash to separate it from aluminium which was dissolved out of the glass.

(5) 0.9465 gramme gave 0.3886 gramme ferric oxide.

* *Loc. cit.*

Several other methods of analysis were also tried, such as decomposing the carbonyl by heat, weighing the iron and measuring the carbon monoxide. A small bulb containing a weighed quantity of the purified iron carbonyl was placed inside a strong glass bulb, a glass tap was then sealed on to this, the bulb exhausted with a Töpler pump, the small bulb was broken and the carbonyl decomposed by heating to about 180° to 200° C., until no deposit of iron could be produced by heating a clear portion of the large bulb with a blow-pipe flame.

The carbon monoxide was then removed, by means of a Töpler pump, and measured; the bulb with the deposited iron was weighed, the iron dissolved off and the bulb weighed again after drying. In this process it was found that the glass was often attacked where the iron had been deposited and the high values obtained for the iron are doubtless to be attributed to this cause, and to the presence of carbon in the iron (see later). The following example illustrates the kind of result obtained by this method:—

- (6) 0.4626 gramme gave 287 c.c. of carbon monoxide at 19° C. and 757 mm. and left 0.1371 gramme of iron.

	Fe.	CO.	CO by volume for 1 gramme.
Found—			
(1)	—	71.2	—
(2)	—	70.9	—
(3)	29.2	—	—
(4)	28.7	—	—
(5)	28.7	—	—
(6)	29.6	—	—
Calculated for $\text{Fe}(\text{CO})_5$	28.57	71.43	564.2 c.c. at 0° C. of 760 mm.
„ $\text{Fe}(\text{CO})_4$	33.33	66.66	571.4 c.c.
			530.9 c.c.

The compound is therefore $\text{Fe}(\text{CO})_5$.

Attempts were made to determine the ratio Fe : CO in the compound by passing nitrogen through a weighed or unweighed quantity of pure iron carbonyl and then through a glass tube bent twice on itself and heated in a bath so that the vapour was heated for some time and decomposed into iron and carbon monoxide; the iron was deposited in the tube and then weighed, the carbon monoxide was passed over hot copper oxide and weighed as carbon dioxide in a potash tube. It had been found previously that this process gave good results in the case of nickel carbonyl.

With iron carbonyl, however, consistent results could never be obtained. In the first place the compound is much more difficult to decompose completely than nickel carbonyl, and it was found that, in order to ensure complete decomposition, it was necessary, when keeping the bath at

180° to 200° C., to heat a small portion of the tube nearer the copper oxide tube nearly to redness. Even then it was always found that the sum of the weights of the iron and carbon monoxide was always less than that of the iron carbonyl taken. This was traced to the fact that the iron deposited was always contaminated with carbon, which was given off as hydrocarbons when the iron was dissolved in acids; also the weight of ferric oxide obtained from the iron was always less than it should have been. The ratio CO : Fe was usually about 4.5 to 4.8; this is readily accounted for by a small percentage of carbon in the iron. The presence of carbon in the iron would also tend to raise the percentage of iron as estimated by method (6).

Further evidence in support of the formula $\text{Fe}(\text{CO})_5$ was afforded by experiments on the decomposition of the vapour enclosed in a space at a given pressure and measuring the pressure of the carbon monoxide produced; this was approximately five times the original pressure of the vapour. These experiments will be referred to later.

Molecular Weight.—Numerous vapour-density determinations have been made and will be described in another part of this paper. When no dissociation occurs the vapour density varied between 98 and 100, so that the molecular weight corresponds to the formula $\text{Fe}(\text{CO})_5$ with a molecular weight of 198.

Two determinations of the molecular weight in benzene were made by the cryoscopic method: a weighed quantity of liquid in a bulb was broken under the benzene. Owing to the very great sensitiveness of the compound to air and moisture, the solution always began to turn turbid before the end of the experiment, even when the greatest care was taken to exclude moisture and the air in the apparatus had been replaced as completely as possible by nitrogen or carbon monoxide.

0.2956 gramme in 14.28 gramme benzene gave a depression of 0.524° C.

Hence the molecular weight is 197.

0.3900 gramme in 14.20 grammes benzene gave a depression of 0.705° C.

Hence the molecular weight is 194.

Specific Gravity of the Liquid.—Mond and Langer* gave the density of liquid iron carbonyl as 1.4664 at 18° C. compared to water at the same temperatures, or 1.4688 compared to water at 4° C. Gladstone† gave the density at 13.4° C. as 1.474, at 15.5° C. as 1.470, and at 22° C. as 1.460.

The specific gravity was determined with the aid of a small glass pyknometer (volume 2.2 c.c.) at temperatures from 0° C. to 80° C. Great care

* *Loc. cit.*

† 'Phil. Mag.,' 1893, [5], vol. 35, p. 204.

was exercised to exclude moisture, and the experiments were carried out in a dim light; a very small amount of decomposition, indicated by the formation of minute bubbles of gas, always took place, which was more marked at the higher temperatures, and was doubtless caused by traces of moisture and air, so that the numbers obtained can only be regarded as approximate for the two highest temperatures. The specific gravity is in each case referred to water at 4° C.

Temp.	Sp. gr.
0·0° C.	1·494
16·5° C.	1·468
40·0° C.	1·421
61·5° C.	1·382
80·0° C.	1·351

These specific gravity determinations were made with a specimen of the carbonyl kindly supplied by Dr. Mond. When a much larger quantity was available this was purified, and further determinations were made with a much larger pyknometer (volume 7·1100 c.c.), using the same precautions (in this case there were no signs of any decomposition).

Temp.	Sp. gr.
0·0° C.	1·4937
21·1° C.	1·4565
40·0° C.	1·4330
60·0° C.	1·3825

These results agree fairly well with those given above, but are naturally more trustworthy on account of the larger quantity of material used.

The coefficient of expansion for 0° C. to 21° C. is 0·00121, for 21° C. to 40° C. is 0·00128, and for 40° C. to 60° C. is 0·00142. The mean coefficient of expansion is, therefore, about 0·00138.

By extrapolation on the curve the specific gravity at the boiling point, 102°·5 C., is 1·310. The molecular volume is, therefore, 149·6. At the melting point, -20° C., the specific gravity is 1·53 and the volume of the molecule is then about 128.

The values of the specific gravity of the liquid at 0° C. and 60° C., taken with the critical temperature (288° C., for which see p. 565), give the following Waterston formula for the relation between the volume v and the temperature t ° C.:—

$$v = 1·974 - 0·5307 \log (288 - t).$$

Refractive Indices.—Gladstone* determined the refractive indices of the carbonyl for several of the lines of the spectrum and found that, as in the case of nickel carbonyl, the compound had a very large molecular refractive power and an enormous dispersive power. It was, therefore, unnecessary to investigate this property minutely, and two determinations only were made for sodium and thallium light with an Abbé refractometer by Mr. A. Hutchinson of the Mineralogical Department.

μ for Na light	1.519
μ „ Tl „	1.528 at 22° C.

These values agree very closely with those found by Gladstone—1.5180 and 1.5289.

Melting Point.—The pale yellow liquid crystallises when cooled to a pale yellow solid which melts at $-19^{\circ}5$ C. to -20° C. At the temperature of liquid air the solid entirely loses its colour, which it gradually recovers on warming up again.

Vapour Pressure and Boiling Point.—The vapour pressure was determined by the statical method as in the case of nickel carbonyl.

A wide barometer tube, drawn off to a fine capillary at one end, was carefully cleaned and placed upright in a vessel of pure dry mercury, in a room lighted by a feeble gas jet. A small tube containing iron carbonyl was now introduced, the whole exhausted thoroughly by means of a Fleuss pump and sealed off at the end. The pressure was then read off by means of a kathetometer, while the tube was surrounded by a bath at various temperatures. Observations taken after cooling and allowing the tube to stand showed that no appreciable amount of decomposition took place under the conditions of the experiment. The results are appended below :—

Temp.	Pressure.
-7.0° C.	14.0 mm.
0.0° C.	16.0 „
16.1° C.	25.9 „
18.4° C.	28.2 „
35.0° C.	52.0 „
57.0° C.	133.0 „
78.0° C.	311.2 „

Next day at $18^{\circ}9$ C. the pressure was 29.4 mm.

The boiling point given by Mond and Langer is $102^{\circ}8$ C. at 749 mm. Several determinations of the boiling point were made, all of which gave a

* *Loc. cit.*

result slightly lower than this. Thus, it was found that the liquid boiled at $101^{\circ}8$ C. at 736 mm., at $102^{\circ}0$ C. at 744 mm. and at $102^{\circ}7$ C. at 764 mm. The values for 0° C. and $102^{\circ}7$ C. give the following Rankine formula for the relation between the vapour pressure p in millimetres of mercury and the absolute temperature T : $\log p = 7.349 - 1681/T$. This fits in very well with the results for the intermediate temperatures.

Critical Temperature.—It was found by trial experiments that the liquid could be heated in a glass tube under pressure to temperatures considerably above its boiling point without undergoing noticeable decomposition. Its critical temperature was, therefore, determined by placing some liquid in small thick-walled capillary tubes, exhausting, sealing-off, and then heating the tubes in an air or paraffin bath until the meniscus disappeared. The tubes were about one-third to one-half full of liquid, and though no deposit of iron was produced, yet the tubes burst after heating several times to the critical point. In several determinations it was found that the meniscus disappeared between 285° C. and 288° C.

The formula $T = 0.66 T_c$, where T_c is the absolute boiling point and T the absolute critical temperature, is usually applicable to liquids which are not associated in the liquid or gaseous state near the boiling point, and was found to be applicable to nickel carbonyl; it should, therefore, be applicable here. Taking the boiling point as $102^{\circ}5$ C., the critical temperature should be $289^{\circ}2$ C., a value agreeing very closely with the number found experimentally.

The critical density of iron carbonyl is calculated to be 0.49, the value for nickel carbonyl is 0.46. The critical pressure calculated from the Rankine formula for the vapour pressure is 29.6 atmospheres.

The number obtained by dividing the absolute critical temperature by the critical pressure, which is proportional to the volume of the molecule, Van der Waals' constant b , is 18.9, the corresponding value for nickel carbonyl is 15.5 and the value for carbon monoxide is 3.7. Hence the volume of the molecule of iron carbonyl is 5.1 times larger than that of carbon monoxide, while 4.2 represents the ratio for the nickel carbonyl.

The latent heat of iron carbonyl is 39.45 calories per gramme, and the Trouton constant, molecular latent heat divided by absolute boiling point, is 20.6, a value identical with that for nickel carbonyl.

The molecular volume of iron carbonyl at its boiling point is 150, so that taking 7.0 as the volume of the iron atom, we get 28.6 as the volume of each carbon monoxide molecule, a number smaller than that found for nickel carbonyl, i.e., 32.2. Liquid carbon monoxide at its boiling point has a molecular volume of 35, so that a greater contraction would take place in

the formation of liquid iron carbonyl from liquid carbon monoxide and iron, if that were possible, than in the formation of nickel carbonyl under similar conditions.

The similarity between many of the constants of nickel and iron carbonyls is very striking, in spite of the fact that the substances differ so widely in their boiling points and stability.

Vapour Density and Dissociation.—Two vapour-density determinations were made by Mond and Langer* by V. Meyer's method in an atmosphere of hydrogen at the temperature of boiling xylene. The results were 93.8 and 92.4, the theoretical value is 98, so that slight dissociation is indicated.

A number of trial experiments showed that iron carbonyl vapour dissociated quietly without explosion when heated to a high temperature alone or in an inert gas.

A series of vapour-density determinations were made by V. Meyer's method in various gases at different temperatures in order to show the effect of temperature, of admixture with inert gas or carbon monoxide and of the rate of diffusion on the dissociation of iron carbonyl. Owing, however, to the great stability of the iron compound and its slow rate of dissociation, these effects are not so clearly seen as in the case of nickel carbonyl. In fact, so slowly does iron carbonyl dissociate, that accurate determinations can only be obtained at the lowest temperatures where no dissociation occurs, and at the highest temperatures where complete dissociation is rapid; at the intermediate temperatures the dissociation is so slow that diffusion to the cooler parts of the tube takes place and the end-point of the evolution of gas is extremely uncertain.

Several series of determination of the vapour density were also made by Hofmann's method to show the effect of pressure and temperature on the dissociation of iron carbonyl; but again, owing to the slow rate of dissociation, the experiments had to be prolonged for an inconveniently long time before even an approximately constant volume was obtained. In these experiments it is advisable to protect the vapour as far as possible from light, since the decomposition of the iron carbonyl by light, which takes place at low temperatures, is thus minimised.

The results obtained are tabulated below. The percentage dissociation is calculated by means of the formula

$$p = \frac{D-d}{4d} 100.$$

* *Loc. cit.*

Vapour Densities determined by Meyer's Method.

Temperature of the bulb.	Gas filling the tube.	Vapour density (H = 1).	Percentage of $\text{Fe}(\text{CO})_5$ dissociated.	Remarks.
129° C. (amyl alcohol)	Carbon monoxide...	98.7	1.2	No visible deposit of iron.
	Nitrogen	98.2		
	Hydrogen	90.1	3.0	Distinct deposit of iron.
		86.2		
		88.7 87.5		
155° C. (turpentine)	Carbon monoxide...	83.6	4.6	Extensive deposit extending over large area of tube
	Nitrogen	78.0	6.4	
		86.4	42.3	
182° C. (aniline)	Carbon monoxide...	44.9	30.1	"
	Nitrogen	44.0		
		27.4	64.4	"
216° C. (naphthalene)	Carbon monoxide...	20.2	96.3	"
	Nitrogen	20.0	97.5	"

Vapour Densities by Hofmann's Method.

Temperature.	Pressure.	Vapour density (H = 1) _v .	Percentage of $\text{Fe}(\text{CO})_5$ dissociated.	Remarks.
78° C.	195	99.8	—	No visible deposit of iron.
	195	98.4	—	
	212	100.0	—	
	288	99.8	—	
100° C.	126	98.3	—	
	179	98.6	—	
	204	97.2	—	
	225	97.1	—	
	298	99.5	—	
130° C.	136	95.0	0.3	
	192	95.7	0.6	
	216	96.2	0.5	
	242	94.5	0.9	
	325	95.0	0.8	
141° C.	261	86.6	3.3	Extremely faint deposit of iron.
155—160° C.	274	70.2	9.9	
	354	88.1	2.31	
179° C.	240	40.4	35.6	Very extensive deposit of iron; on cooling much undecomposed iron carbonyl condensed
	334	40.4		
	406	44.2	30.2	
	574	45.6	28.8	

These results show very clearly the effect of increase of temperature and of diminution of pressure in increasing the dissociation, the effect of carbon

monoxide in diminishing the dissociation observed in an inert gas at the same temperature. The increased dissociation in a light inert gas as compared with a heavy one is shown by the values in hydrogen and nitrogen at 129° C.

The rate of dissociation of the vapour at various temperatures was also studied in an apparatus very similar to that used by Mittasch* for the dissociation of nickel carbonyl. Owing to the small vapour pressure of iron carbonyl the range of pressures of undissociated vapour is very limited.

The rate of dissociation is very slow at temperatures below 180° C., but appears to be complete at that temperature. The reaction is reversible, but the reversal takes place very slowly.

Chemical Reactions of Iron Pentacarbonyl.—An examination of some of the simpler reactions of iron carbonyl was made in order to study its chemical nature and stability in comparison with nickel carbonyl, the reactions of which have already been described.† The action of the halogens in solution in pure dry carbon tetrachloride on normal and decinormal solutions of iron carbonyl in the same solvent was first investigated; the solutions were mixed in a nitrometer and allowed to stand, the gas evolved measured and tested and the solid examined.

Chlorine and iron carbonyl react fairly rapidly to produce a solid and carbon monoxide, which was measured, and showed that the decomposition was complete. The solid was found to be a mixture of ferrous and ferric chlorides, the ferrous chloride could never be obtained quite free from ferric, but by using a large excess of chlorine practically pure ferric chloride could be obtained. The gas appeared to be practically pure carbon monoxide and to contain no carbonyl chloride.

Bromine reacts with iron carbonyl very slowly, in fact much more slowly than iodine reacts with nickel carbonyl. Five c.c. of a decinormal solution of iron carbonyl and 1 c.c. of normal bromine solution should evolve 22.4 c.c. of gas, 15 c.c. of gas had been evolved in six hours, 19.5 c.c. in 20 hours, and the reaction was practically complete in 35 hours. The solid salt consisted chiefly of ferrous bromide with minute traces of ferric salt, the gas was pure carbon monoxide. This reaction shows the much greater stability of the iron compound over the nickel compound, which is decomposed by bromine in a few seconds after mixing.

Iodine reacts extremely slowly with iron carbonyl to produce carbon monoxide and ferrous iodide; in decinormal solution the reaction had only proceeded to the extent of 70 per cent. in three days.

Iodine monochloride in chloroform solution reacts with iron carbonyl much

* 'Zeit. Phys. Chem.,' 1902, vol. 40, p. 1.

† 'Trans. Chem. Soc.,' 1904, vol. 85, pp. 203—222.

in the same way as it does with nickel carbonyl; ferrous chloride is precipitated and iodine liberated, the solution becoming purple, the free iodine then reacts very slowly with the residual iron carbonyl.

The whole reaction is a very slow one, and the salt at first precipitated is ferrous chloride with no trace of ferric salt and no iodide, a little iodide appears before the formation of chloride is complete, but no ferric salt is produced.

Iodine trichloride in chloroform solution reacts slowly with iron carbonyl, producing a solid deposit and evolving gas; no free iodine is produced for a long time. The solid is again ferrous chloride free from ferric chloride, and contains very little iodide until the reaction has been proceeding for some time.

Cyanogen gas does not appear to react at all with iron carbonyl liquid or vapour, and in alcohol solution the reaction is extremely slow.

Cyanogen iodide in chloroform solution reacts very gradually, the solution first becoming red and then purple and a brown solid is deposited. The solvent contains free iodine and the solid is ferrous cyanide mixed with a little ferrous iodide.

The action of the halogen hydrides was examined in the gaseous state and also in chloroform solutions.

Hydrochloric and *hydrobromic acid* gases had no action on iron carbonyl even after allowing the mixture to stand for weeks in the dark. Dry *hydriodic acid* gas was introduced into an exhausted glass bulb containing a small glass bulb full of iron carbonyl, which was then broken. On standing, a dark brown crystalline solid was produced, which was found to be ferrous iodide, and at the same time carbon monoxide and hydrogen were liberated.

In chloroform solution hydrochloric acid and hydrobromic acid react slowly with iron carbonyl, the former more slowly than the latter. In each case pure ferrous salts were produced and hydrogen and carbon monoxide were evolved. With a chloroform solution of hydriodic acid the reaction was more rapid and was complicated as in the case of nickel carbonyl by the liberation of iodine.

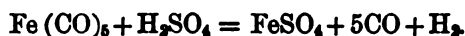
The reactions of iron carbonyl described above are exactly parallel with the corresponding reactions of nickel carbonyl, only differing in rapidity, which is much less owing to the greater stability of the iron compound. There is a more marked difference to be observed in some of the other reactions.

With *sulphur* dissolved to carbon bisulphide or xylene, iron carbonyl does not react at all in the cold, neither does it react with *nitric oxide*, in both cases differing markedly from nickel carbonyl.

Hydrogen sulphide also has no action on iron carbonyl, but an alcohol solution of the gas reacts extremely slowly to produce ferrous sulphide, carbon monoxide and hydrogen.

Nitric acid in carbon tetrachloride or ether solution reacts rapidly with iron carbonyl to produce a mixture of ferrous and ferric nitrates, carbon monoxide with some hydrogen and reduction products of nitric acid.

Concentrated sulphuric acid reacts rapidly with iron carbonyl, the mixture first darkens, carbon monoxide and hydrogen are evolved, mixed with a little iron carbonyl vapour; the liquid then becomes paler in colour as the reaction is completed. The salt formed is pure ferrous sulphate, so that the reaction may be expressed by the following equation :—



The rapidity of the reaction is very much greater than in the case of nickel carbonyl; this is the only reaction yet observed which is more rapid than the corresponding reaction with nickel carbonyl.

To complete the comparison between the nickel and iron compounds in so far as the reactions of nickel carbonyl have been described, the reaction of iron carbonyl with *benzene* in presence of *aluminium chloride* was examined. Four grammes of iron carbonyl and 10 grammes benzene (five molecules) were poured on to 28 grammes powdered aluminium chloride (five molecules) in a tube, which was then sealed off and heated for two hours to 100° C. The mixture became very dark in colour, and on opening the tube some pressure caused by carbon monoxide and a little hydrochloric acid gas was observed.

The dark mass was mixed with ice, when some ferrous chloride dissolved and some ferrous hydroxide was precipitated, treated with hydrochloric acid and distilled in steam. Benzaldehyde and benzene came over first followed by a crystalline fluorescent solid; the residue in the flask was dissolved in benzene, dried and distilled, when a crystalline solid was obtained which was found to be pure anthracene, so also was the small quantity of solid which distilled in steam.

The final products of the reaction in this case are, therefore, precisely the same (namely, benzaldehyde and anthracene) as those produced by using nickel carbonyl. In the cold the reaction proceeds slowly, with the production of benzaldehyde and no anthracene, again precisely as in the case of nickel carbonyl.

Decomposition by Light.—Mond and Langer* state that liquid iron carbonyl is rapidly decomposed by light, giving rise to a solid product and

* *Loc. cit.*

carbon monoxide. Determinations of the percentage of iron in the compound made by them indicated that the formula was $\text{Fe}_2(\text{CO})_7$, but the body was not obtained in a pure state. This behaviour to light constitutes the most striking difference between the carbonyls of iron and nickel, and was therefore examined more fully.

The decomposition was first investigated over mercury in a barometer tube. A weighed quantity of liquid iron carbonyl in a sealed bulb was introduced into a barometer and the bulb was then broken, after which the tube was exposed to light.

In the laboratory on bright days in February the decomposition was extremely slow, but on the same days in direct sunlight the decomposition was rapid and the evolution of gas was completed in a few hours. Exposure to the electric arc only induces the change very slowly, and a strong acetylene flame is almost without action. The volume of gas evolved (which was found to be pure carbon monoxide) was then measured and the solid collected. The solid was found to consist of beautiful, lustrous, hexagonal plates of an orange colour, which, when pure, retained their lustre for a very long time on exposure to ordinary air, and indefinitely in dry air; if, however, the decomposition had not been completed and the solid was contaminated with traces of the liquid compound, rapid change occurred and the compound sometimes took fire.

The following are two typical examples of experiments made in this way:—

- | | | | | | |
|-----|--------|----------------------|------|------|--------------------------|
| (1) | 0.0905 | gramme iron carbonyl | gave | 4.7 | c.c. of carbon monoxide. |
| (2) | 0.2970 | " | " | 18.4 | " " |

According to the equation



there should have been produced 15.5 c.c. and 50.9 c.c. of carbon monoxide respectively, whereas the equation



requires 5.2 c.c. and 17 c.c. of carbon monoxide respectively.

It would, therefore, appear that the formula of the solid compound is $\text{Fe}_2(\text{CO})_9$ and not $\text{Fe}_2(\text{CO})_7$, and that the decomposition induced by light is represented by equation (2) above. This result was confirmed by carrying out the decomposition in a large glass bulb out of contact with mercury.

A small sealed bulb filled with iron carbonyl was introduced into a large glass bulb, which was then sealed on to a glass tap, dried carefully,

and exhausted with a Töpler pump. The small bulb was then broken and the whole exposed to light for some days, after which the carbon monoxide was pumped out and measured. In these experiments it was practically impossible to get the decomposition completed, since the bulb became covered with a deposit of the solid, which cut off the light.

The following are typical examples :—

0.6006 gramme of the liquid carbonyl gave 33.2 c.c. of carbon monoxide and left 0.501 gramme of solid. Theory requires 34.3 c.c. of gas and 0.557 gramme of solid.

0.5076 gramme gave 32 c.c. of gas. Theory requires 33.8.

Decomposition was incomplete, as shown by behaviour of solid, and by the fact that on admitting air to the carbon monoxide a deposit of iron oxide was produced. Another type of experiment also served to confirm the above conclusively :—

A carefully dried glass bulb of about 250 c.c. capacity was fitted with a small mercury manometer, thoroughly exhausted, and filled with dry iron carbonyl vapour, the pressure of which was measured at a definite temperature. The bulb was then exposed to light until no further change took place; after the bulb had been brought to the original temperature, the pressure was found to have been reduced to one-half its former value, as required by equation (2) above.

None of the specimens of the solid carbonyl prepared by either of the foregoing methods was found to be pure enough to give good results on analysis. The specimens prepared over mercury always retained small globules of mercury too small to be visible, but whose presence became evident during combustion, while the specimens prepared in glass bulbs were always contaminated with a little of the liquid, which either caused spontaneous combustion of the sample or decomposed quietly and left some oxidation product poor in carbon. The percentages of carbon monoxide obtained were too high for $\text{Fe}_2(\text{CO})_7$, 63.6 per cent, and too low for $\text{Fe}_2(\text{CO})_9$, 69.2 per cent.; thus, for example, 65.0 and 66.5 per cent. of carbon monoxide were obtained in two combustions.

We therefore examined the decomposition of the liquid in various solvents and succeeded in obtaining the compound in a pure state.

Iron pentacarbonyl dissolved in dry ether or petroleum ether and exposed to sunlight, undergoes rapid decomposition with evolution of carbon monoxide and formation of large reddish orange crystals of the solid carbonyl. To obtain the pure solid compound in quantity, the solution was sealed up in a dried and exhausted glass tube, and exposed to light. Owing to the unavoidable exposure to air during the transference, a small amount of a precipitate

of an oxidation product was sometimes produced. When a quantity of the solid carbonyl had been formed, the tube was opened (a considerable pressure of carbon monoxide was always produced), and the precipitate was removed easily by shaking the tube and pouring off the liquid, when the precipitate, which is very light and settles slowly, is poured off with the liquid, and the crystals remain behind. The crystals were then washed two or three times with the solvent and rapidly transferred to a desiccator containing sulphuric acid and solid paraffin. When prepared in this way they retain their lustre, and show no signs of change for a long time on exposure to air.

The percentage of carbon monoxide was then determined by combustion, using the same precautions as in the case of the liquid. The method of estimating the iron after decomposing the solid by heating in a sealed tube with bromine water was found unsatisfactory, and after trying several methods it was found that, if the compound were dropped slowly into pure nitric acid in a weighed crucible, complete decomposition took place, with effervescence and without loss of iron. The resulting liquid was then evaporated to dryness on a water bath, the ferric nitrate decomposed by careful ignition, and the ferric oxide weighed.

The following results were obtained by these methods:—

	(1)	0.2470	gramme	gave	0.2655	gramme	CO ₂ .
	(2)	0.3178	"	"	0.3417	"	"
	(3)	0.1839	"	"	0.1992	"	"
	(4)	0.5791	"	"	0.2534	gramme	Fe ₂ O ₃ .
	(5)	0.3450	"	"	0.1515	"	"

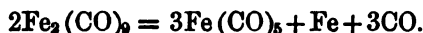
Found—

	CO.	Fe.
(1).....	68.4	—
(2).....	68.4	—
(3).....	68.9	—
(4).....	—	30.6
(5).....	—	30.7
Fe ₂ (CO) ₇ requires ...	63.60	36.40
Fe(CO) ₄ " ...	66.66	33.33
Fe ₂ (CO) ₉ " ...	69.20	30.80

The solid compound is therefore Fe₂(CO)₉, or *diferro-nona-carbonyl*. The solid prepared in this way forms large hexagonal plates, often 3 or 4 mm. in breadth, but always rather thin. It is very sparingly soluble, in fact practically insoluble, in ether, petroleum-ether, and benzene, but is slightly soluble in methylal, alcohol and acetone, and much more soluble in pyridine to form a

reddish solution. When dissolved the compound becomes much more sensitive to air and moisture, and deposits a reddish precipitate. We have not yet succeeded in recrystallising the compound. The crystals are slightly diamagnetic, but less so than the liquid. The density of the solid at 18° C. is 2.085, and its molecular volume is therefore about 174. If two grammes-molecules of solid $\text{Fe}(\text{CO})_5$ were converted into $\text{Fe}_2(\text{CO})_9$, then 256 volumes would become 174, or a contraction of about 33 per cent. would ensue.

On heating solid iron carbonyl, as stated by Mond and Langer, liquid iron carbonyl is produced, and some solid, probably iron, is left. We find that this change takes place at about 100° C. Under a pressure of carbon monoxide up to 150 atmospheres, there is no rapid change below 95° C., but at this temperature the solid is completely converted into liquid iron carbonyl, though traces of a yellowish-brown solid are sometimes left. Quantitative experiments were made on the decomposition at 100° C. in a stream of hydrogen, and showed that the decomposition could be represented by the following equation:—



Liquid iron carbonyl, when exposed to light under a pressure of 75 to 125 atmospheres of carbon monoxide in the tube of a Cailletet pump, decomposes without any apparent diminution of the rate of transition. For this purpose the liquid was placed in a small tube kept in position by a plug of glass wool so that the liquid never came in contact with the mercury. If, however, the sealed tube containing liquid iron carbonyl, or a solution of it in ether, be heated to any temperature between 60° and 100° C., while exposed to light, no solid separates even after several hours, whereas below 50° C. solid is formed in about half an hour. This is also true when the liquid is under a pressure of 50 to 100 atmospheres of carbon monoxide. The solution which had been exposed to light at a temperature above 60° C. even on cooling gave no deposit of solid, showing that no decomposition had been caused by the action of light at these temperatures. And this is confirmed by the fact, which will be proved later, that if solid had been produced in solution it would at this temperature have formed a solution of an intense green colour.

The decomposition of liquid iron carbonyl dissolved in ether, amylene, or petroleum-ether (B.P., 30° to 40° C.) by light, takes place slowly at the temperature of liquid air. The solutions become solid, and, after exposure to sunlight for about three hours inside a vacuum vessel of liquid air, and then allowing to warm up in the dark, a faint deposit of solid was observed.

In spite of the fact that pressure is not effective in preventing the

decomposition by light, the reaction is reversed slowly under a slight pressure of carbon monoxide at the ordinary temperature in the dark. Tubes containing iron carbonyl alone, or in solution, which had been exposed to light so that they contained some of the solid carbonyl, on standing at the ordinary temperature in the dark for some weeks, were found to contain no solid; so that the solid had absorbed the carbon monoxide which had been evolved, and had been completely reconverted into the liquid. These observations are of considerable interest and importance in their bearing on the question as to whether the action of light is exothermic or endothermic. If the light reaction is not endothermic, then we must assume the action of carbon monoxide on the solid carbonyl, and the change backwards into the liquid carbonyl is attended by an absorption of heat. Further experiments must be made to settle the question.

When solid iron carbonyl is heated alone, as stated above, no change takes place below 100°C. , at this temperature a solid and a *green* liquid are formed. But if the solid be heated with liquids such as ether, petroleum-ether, or toluene, change begins at about 50°C. , the solid decomposes and the liquid acquires an intense green colour. The intensity of the green colour is so great that the solutions are almost opaque, even in thin layers; in more dilute solutions the absorption spectrum showed a distinct band in the yellow. These green solutions, on exposure to light, again deposit yellow crystals of the solid carbonyl, and become colourless.

In order to determine what kind of light was most effective in inducing this decomposition, small tubes containing a 10-per-cent. solution of iron pentacarbonyl in ether were exposed in different parts of a solar spectrum and also to sunlight under different coloured screens. It was found that most rapid decomposition occurred in the blue, then green, closely followed by yellow, and lastly red: exposure under red glass produces roughly about one-tenth the amount of solid produced under blue glass in the same time.

Exposure of the liquid in quartz tubes to the electric arc causes slow decomposition only, and the acetylene flame is still less active.

Colouring the ether solution with dyes was also tried; cyanine and chlorophyll allow rapid decomposition, azobenzene retards the decomposition slightly, isatin and alizarine somewhat more.

It has already been stated above that the decomposition occurs readily in solution in petroleum ether and ether; the same is true of alcohol; in pure benzene the decomposition appears to be slower, but if the benzene contain traces of thiophene a black solid is deposited. Solutions of iron carbonyl in pyridine become dark red in colour when exposed to light, gas is evolved, but no solid is deposited except from strong solutions of about 50 per cent. by

volume. This is to be accounted for by the solubility of the solid in pyridine. Carbon bisulphide and nitrobenzene, which do not react with iron carbonyl in the dark, when exposed to light, react, with the formation of solid precipitates.

The most striking result observed was with solutions of iron carbonyl in nickel carbonyl. These solutions are of a much paler yellow colour than solutions of equal concentration in other solvents. Thus for example a 10-per-cent. solution of iron carbonyl in ether has just the same intensity of colour as a 30-per-cent. solution in nickel carbonyl. A 10-per-cent. solution deposits no solid after exposure to bright sunlight for several weeks, a 25-per-cent. solution (by volume) deposits no solid from the liquid, but solid is deposited in the vapour space above the liquid; a 50-per-cent. solution deposits some solid both in the liquid and in the vapour space.

That no decomposition occurs in dilute solutions of iron carbonyl in nickel carbonyl is shown by the facts that no gas is evolved from these solutions, and that solid iron carbonyl is only sparingly soluble in nickel carbonyl. The absence of any change is not to be accounted for by the absorption of the active light by the nickel carbonyl, since the iron carbonyl has been shown above to be sensitive to light in the visible part of the spectrum which is not absorbed by nickel carbonyl. This fact was further confirmed by exposing a small tube full of iron carbonyl immersed in liquid nickel carbonyl to light, when decomposition was found to take place rapidly.

The following may be suggested as a simple hypothesis to account for the unique behaviour of nickel carbonyl as a solvent of iron carbonyl:—

The initial action of light on iron carbonyl might be represented by the equation



the hypothetical iron tetracarbonyl produced may be assumed to combine at once with a molecule of iron pentacarbonyl to produce the solid nona-carbonyl, thus:—



If this molecular mechanism of the light reaction be admitted, then there is no reason why iron pentacarbonyl may not form an analogous body of feeble stability by combining directly with nickel tetracarbonyl, thus:—



A compound of this kind, though unstable in itself (since the vapour above the solutions contains iron carbonyl and the concentrated solutions deposit some solid), may yet be unacted upon by light. The existence of this compound is rendered probable by the fact that solutions of iron carbonyl in

nickel carbonyl have such a pale colour compared to solutions of the same concentration in other solvents.

The observations on the action of light on iron carbonyl under different pressures of carbon monoxide, at different temperatures and in solution in various solvents, will be continued as soon as the necessary sunlight is available.

The Electrical Conductivity of Dilute Solutions of Sulphuric Acid.

By W. C. D. WHETHAM, M.A., F.R.S.

(Received November 8,—Read November 16, 1905.)

§ 1.—*Introduction and Summary of Results.*

If the measure of the electrical conductivity of a solution be divided by that of the concentration expressed in gramme-equivalents per unit volume, we obtain a quantity which may be called the equivalent conductivity of the solution. If the conductivity of the solvent used be subtracted from that of the solution, the corresponding quantity may be taken as giving the equivalent conductivity of the solute.

As is well known, the equivalent conductivity of neutral salts when dissolved in water approaches a limiting value as the dilution is increased, and, in terms of the ionisation theory, this limiting value corresponds with complete ionisation.

With solutions of acids and alkalies, however, the phenomena are different. As dilution proceeds, the equivalent conductivity reaches a maximum at a concentration of about a one-thousandth or a two-thousandth of a gramme-equivalent per litre, and then falls rapidly as the dilution is pushed farther.

It has been supposed that this diminution of equivalent conductivity at extreme dilutions is due to interaction between the solute and the impurities which remain even in redistilled water.

Kohlrausch* has given evidence to show that the chief impurity in water carefully redistilled is carbonic acid, and Goodwin and Haskell† have corrected the observed values of the equivalent conductivity of nitric and

* 'Wissensch. Abhandl. d. phys.-tech. Reichsanstalt,' vol. 3, p. 193 (1900).

† 'Physical Review,' vol. 19, p. 369 (1904).

hydrochloric acids on the assumption that "the total effect of the acid and of the impurities in the water on the conductivity of each other is already produced when a relatively small quantity of acid has been added to the water." These observers conclude that the diminution of equivalent conductivity of dilute acids is due to the presence of carbon dioxide.

In order to examine the real effect of carbonic acid and other impurities on the conductivity of an acid solution, the writer and his wife have carried out an investigation in which the amount of impurity was varied, and the result observed. The conductivity of dilute solutions of sulphuric acid and its variation with concentration was determined in four solvents: (1) good quality redistilled water; (2) the same water to which a trace of carbon dioxide had been added; (3) the same water with a trace of potassium chloride; (4) the same water which had been freed as far as possible from carbonic acid and other volatile impurities by repeated boiling under diminished pressure.

In each case the conductivity of the solvent was subtracted from that of the solution. The results may be summarised as follows:—

Within the limits of experimental error, the equivalent conductivity of a dilute acid is not affected by boiling the water under diminished pressure, though the conductivity of the solvent is thereby much diminished. The equivalent conductivity of the acid is also unaffected by the addition of a small quantity of potassium chloride to the water, though the conductivity of the solvent is thereby much increased. But, by the addition of a little carbonic acid, the equivalent conductivity of the sulphuric acid is diminished appreciably. It is natural to conclude that, while the presence of carbonic acid would produce a diminution of equivalent conductivity of the same character as that observed, it does not explain the total effect.

§ 2.—*The Experiments.*

The solvent used was water kindly prepared by Mr. T. G. Bedford and Mr. W. Spens. It was distilled in a glass still with potassium permanganate and sulphuric acid, and then redistilled in a platinum still with baryta water. It was collected in a large stoppered flask of Jena glass, in which it was kept till used. Its conductivity was about 0.9×10^{-6} or 1.0×10^{-6} in reciprocal ohms per centimetre cube. The best water obtained by Kohlrausch by distillation in air had a conductivity of about 0.7×10^{-6} in these units.

The sulphuric acid was supplied in a sealed glass bulb by Messrs. Baird and Tatlock as chemically pure acid mixed with 50 per cent. of water. For

the purposes of this investigation absolute values of the equivalent conductivity were not needed to very great accuracy. The conductivity of a stock solution (B), prepared by diluting by weight the 50-per-cent. acid, was therefore determined in a resistance cell, and the concentration of the solution calculated from Kohlrausch's results. The constant of the cell was determined by measuring in it the resistance of a solution of potassium chloride, prepared by weighing out a quantity of the pure salt dried by heating in a tube in a current of dry air. The cell constant was found to be 0.1274, a number which, divided by the resistance of the solution in ohms, gave its conductivity in reciprocal ohms per centimetre cube. The concentration of the stock solution (B) was thus estimated as 0.02408 gramme-equivalents per litre. Three other stock solutions (C, D, and F) were also used. They were prepared by diluting B by weight. Their concentrations in gramme-equivalents per litre were:—

(C) 0.002379, (D) 0.005212 and (F) 0.005928.

The cell used for the resistance measurements consisted of a tube of Jena glass about 18 cm. long and 4 cm. in diameter. A rubber cork closed it so as to be airtight, and carried a box-wood core, through which passed two glass tubes supporting the electrodes, and another glass tube for adding stock solution and exhausting the apparatus by means of an air-pump. The electrodes were of stout platinum sheet, and were fixed to thick platinum wires fused through the glass tubes. The electrodes were platinised electrolytically, and then heated to redness. This process gives a rough surface, which does not seem appreciably to absorb electrolytes from a solution.

About 50 grammes of water were placed in the tube cell, which was then weighed. The rubber head was inserted, and the cell placed in a water bath, the temperature of which was kept within a degree or less of 18° C. and observed accurately. The resistance of the water was measured, and corrected to 18° by the known temperature coefficient. Small quantities of stock solution were then added successively, by means of a small vessel of Jena glass, which was weighed before and after each addition.

The resistance measurements were made with alternating currents by means of a resistance box, moving-coil galvanometer, and alternator driven by hand, as described in former papers.* The accuracy of measurement varied as the resistance altered, but was seldom less than one in a thousand.

* 'Phil. Trans.,' A, vol. 259, p. 321 (1900).

First Series. Solvent—Water as redistilled.

No. of solution.	Concentration in gramme-equivalents per 1000 grammes of solution = m_1 .	m_1 .	Resistance at 18° C.	Conductivity = k .	Conductivity corrected for that of solvent.	Equivalent conductivity of sulphuric acid. $\frac{k}{m} = \frac{1000k}{m_1}$.
I. 0	0·0	—	126700	$1·005 \times 10^{-6}$	—	—
1	$2·877 \times 10^{-5}$	0·0806	11850	$1·075 \times 10^{-6}$	$9·74 \times 10^{-6}$	388·6
2	$6·100 \times 10^{-5}$	0·0894	5483	$2·324 \times 10^{-6}$	$2·223 \times 10^{-6}$	364·5
3	$1·416 \times 10^{-4}$	0·0521	2340	$5·445 \times 10^{-6}$	$5·344 \times 10^{-6}$	377·5
4	$2·835 \times 10^{-4}$	0·0658	1182	$1·077 \times 10^{-4}$	$1·067 \times 10^{-4}$	376·4
5	$6·114 \times 10^{-4}$	0·0848	559·5	$2·277 \times 10^{-4}$	$2·267 \times 10^{-4}$	370·8
II. 0	0·0	—	187800	$9·083 \times 10^{-7}$	—	—
1	$2·487 \times 10^{-5}$	0·0292	14120	$9·024 \times 10^{-6}$	$8·121 \times 10^{-6}$	336·9
2	$4·618 \times 10^{-5}$	0·0859	7434	$1·714 \times 10^{-5}$	$1·624 \times 10^{-5}$	352·0
3	$1·097 \times 10^{-4}$	0·0479	8051	$4·177 \times 10^{-5}$	$4·087 \times 10^{-5}$	372·7
4	$2·446 \times 10^{-4}$	0·0625	1371	$9·295 \times 10^{-5}$	$9·205 \times 10^{-5}$	376·3
5	$4·298 \times 10^{-4}$	0·0755	791	$1·611 \times 10^{-4}$	$1·602 \times 10^{-4}$	372·7
6	$9·304 \times 10^{-4}$	0·0976	372·9	$3·417 \times 10^{-4}$	$3·408 \times 10^{-4}$	366·3
7	$1·872 \times 10^{-3}$	0·1233	194·6	$6·549 \times 10^{-4}$	$6·540 \times 10^{-4}$	349·3

Second Series. Solvent—Water with Trace of Carbonic Acid added.

Original water..... Resistance = 129700 ohms at 18°.

Conductivity = $9·622 \times 10^{-7}$.After passage of CO₂ ... Resistance = 34200 ohms at 18°.Conductivity = $3·726 \times 10^{-6}$.

No. of solution.	Concentration in gramme-equivalents per 1000 grammes of solution = m_1 .	m_1 .	Resistance at 18° C.	Conductivity = k .	Conductivity corrected for that of solvent.	Equivalent conductivity of sulphuric acid. $\frac{k}{m} = \frac{1000k}{m_1}$.
I. 0	0·0	—	34200	$3·726 \times 10^{-6}$	—	—
1	$3·722 \times 10^{-5}$	0·0334	8676	$1·469 \times 10^{-5}$	$1·096 \times 10^{-5}$	394·5
2	$7·515 \times 10^{-5}$	0·0422	4441	$2·868 \times 10^{-5}$	$2·495 \times 10^{-5}$	332·1
3	$1·765 \times 10^{-4}$	0·0561	1890	$6·740 \times 10^{-5}$	$6·367 \times 10^{-5}$	360·8
4	$4·165 \times 10^{-4}$	0·0747	808·8	$1·576 \times 10^{-4}$	$1·539 \times 10^{-4}$	369·5
5	$8·969 \times 10^{-4}$	0·0964	384·1	$3·318 \times 10^{-4}$	$3·281 \times 10^{-4}$	365·8
6	$1·868 \times 10^{-3}$	0·1231	193·1	$6·599 \times 10^{-4}$	$6·562 \times 10^{-4}$	351·3
II. 0	0·0	—	43800	$2·908 \times 10^{-6}$	—	—
1	$3·529 \times 10^{-5}$	0·0321	9447	$1·349 \times 10^{-5}$	$1·058 \times 10^{-5}$	299·9
2	$8·990 \times 10^{-5}$	0·0448	3730	$3·416 \times 10^{-5}$	$3·125 \times 10^{-5}$	347·5
3	$2·225 \times 10^{-4}$	0·0606	1511	$8·431 \times 10^{-5}$	$8·140 \times 10^{-5}$	366·7
4	$5·192 \times 10^{-4}$	0·0804	653·1	$1·951 \times 10^{-4}$	$1·922 \times 10^{-4}$	370·1

Third Series. Solvent—Water with Trace of Potassium Chloride added.

Original water..... Resistance = 132000 ohms at 18°.

Conductivity = 9.652×10^{-7} .

After addition of salt... Resistance = 53640 ohms at 18°.

Conductivity = 2.367×10^{-6} .

No. of solution.	Concentration in gramme-equivalents per 1000 grammes of solution = m_1 .	m_1 .	Resistance at 18° C.	Conductivity = k .	Conductivity corrected for that of solvent.	Equivalent conductivity of sulphuric acid. $\frac{k}{m} = \frac{1000k}{m_1}$.
0	0.0	—	53640	2.367×10^{-6}	—	—
1	3.010×10^{-5}	0.0311	10400	1.225×10^{-6}	9.88×10^{-6}	328.2
2	5.854×10^{-5}	0.0388	5485	2.323×10^{-6}	2.086×10^{-6}	356.4
3	1.271×10^{-4}	0.0508	2565	4.966×10^{-6}	4.729×10^{-6}	372.2
4	2.638×10^{-4}	0.0641	1251	1.0186×10^{-4}	9.949×10^{-6}	377.1
5	5.888×10^{-4}	0.0776	717.4	1.776×10^{-4}	1.752×10^{-4}	374.5
6	9.975×10^{-4}	0.0999	348.2	3.658×10^{-4}	3.634×10^{-4}	364.8

Fourth Series. Solvent—Water boiled under low pressure.

Original water..... Resistance about 130000 ohms at 18°.

Conductivity „ 9.8×10^{-7} .

After five exhaustions Resistance = 233200 ohms at 18°.

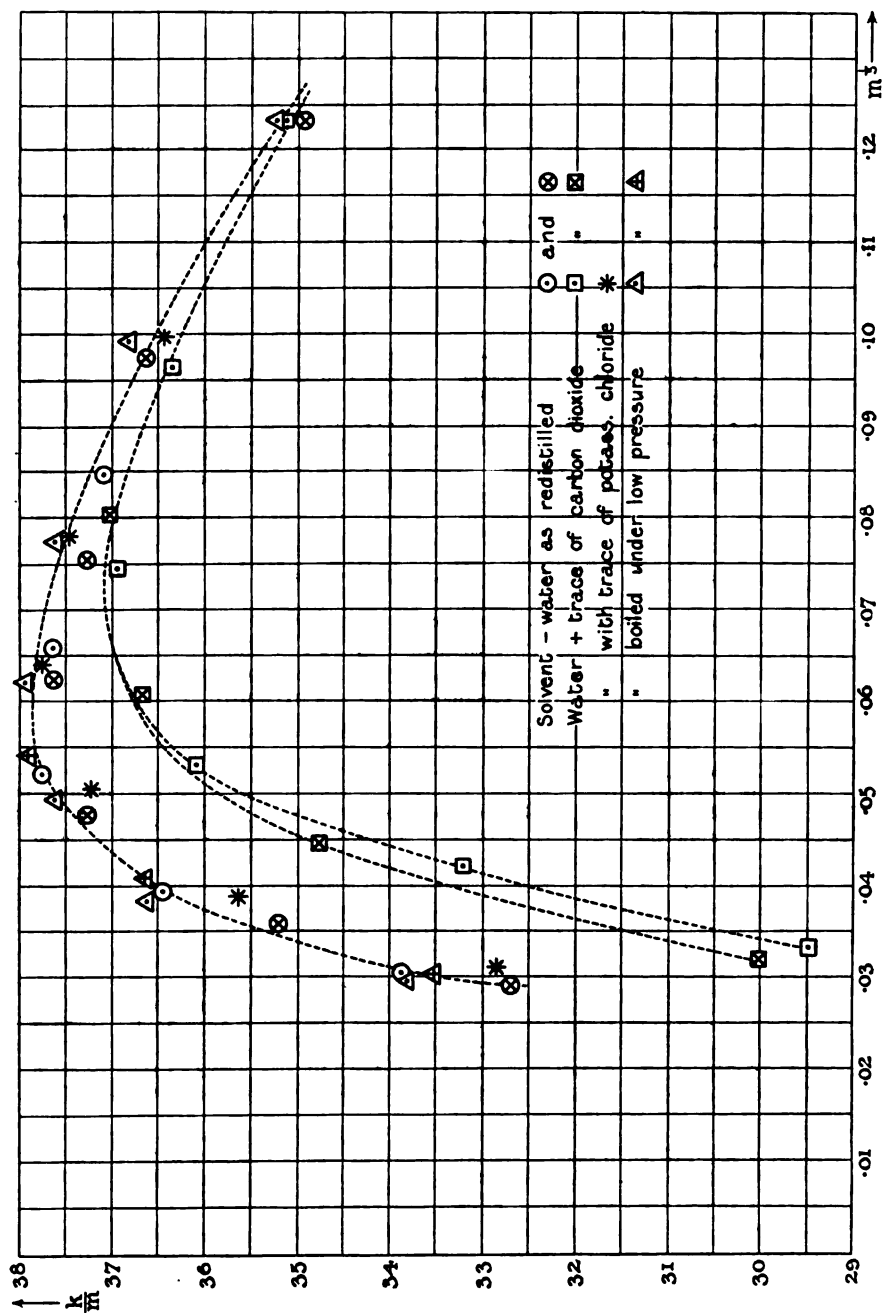
Conductivity = 5.709×10^{-7} .

No. of solution.	Concentration in gramme-equivalents per 1000 grammes of solution = m_1 .	m_1 .	Resistance at 18° C.	Conductivity = k .	Conductivity corrected for that of solvent.	Equivalent conductivity of sulphuric acid. $\frac{k}{m} = \frac{1000k}{m_1}$.
I. 0	0.0	—	233200	5.709×10^{-7}	—	—
1	2.590×10^{-5}	0.0297	13670	9.322×10^{-8}	8.751×10^{-6}	337.9
2	5.653×10^{-5}	0.0384	5999	2.125×10^{-6}	2.068×10^{-6}	365.9
3	1.189×10^{-4}	0.0493	2814	4.528×10^{-6}	4.471×10^{-6}	375.9
4	2.417×10^{-4}	0.0622	1382	9.220×10^{-6}	9.163×10^{-6}	379.2
5	4.609×10^{-4}	0.0773	732.8	1.739×10^{-4}	1.733×10^{-4}	375.9
6	9.738×10^{-4}	0.0991	355.2	3.588×10^{-4}	3.582×10^{-4}	367.8
7	1.864×10^{-3}	0.1231	193.9	6.570×10^{-4}	6.564×10^{-4}	352.2
II. 0	0.0	—	199000	6.401×10^{-7}	—	—
1	2.830×10^{-5}	0.0305	12580	1.012×10^{-6}	9.48×10^{-6}	335.0
2	6.670×10^{-5}	0.0406	5083	2.507×10^{-6}	2.443×10^{-6}	366.2
3	1.604×10^{-4}	0.0543	2078	6.146×10^{-6}	6.082×10^{-6}	378.8

§ 3.—Conclusions.

It will be noticed that the curve for solutions of sulphuric acid in water containing a trace of potassium chloride is hardly appreciably different from

that for water alone, while the addition of a little carbon dioxide to the



solvent results in a curve which is markedly different from the water curve. It must be remembered, however, that, although the conductivity of the

solvent was increased to about the same extent by adding potassium chloride and carbon dioxide, the latter is very slightly ionised, so that a much greater equivalent amount of carbonic acid than of potassium chloride was present.

The addition of an impurity, which is certainly present to some extent in redistilled water, is thus seen to increase the effect we are investigating. The diminution of equivalent conductivity is more marked, and the maximum of the curve is reached at a higher concentration. At this stage of the work it seemed possible that the whole effect might be explicable by the interaction of the acid with the impurities of the solvent.

The next step was to remove as much as possible of the residual carbon dioxide from a sample of the purest water obtainable. The water was placed in the tube-cell, and the air above it exhausted as completely as possible, the water boiling freely under the low pressure. Air was then re-admitted through tubes filled with small lumps of caustic potash to absorb the carbon dioxide. This operation of exhaustion was repeated five times. The conductivity was reduced by this means from 0.98×10^{-6} to 0.57×10^{-6} . The usual additions of sulphuric acid were then made. The resulting curve, shown in the diagram by spots and crosses in triangular frames, is not appreciably different from that obtained with the usual water as solvent.

This result seems conclusive against the supposition that the abnormally low equivalent conductivity of very dilute solutions of acids is wholly due to the presence of carbon dioxide as an impurity in the water used as solvent. The effect of saline impurities, too, of the type of potassium chloride, seems incapable of explaining the phenomenon.

At the first opportunity further experiments will be undertaken to investigate the influence of possible slight traces of ammonia, and, if this proves insufficient to explain the phenomenon, to examine the question from other points of view.

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Hahn (O.) A New Radio-active Element which evolves Thorium Emanation. Preliminary Communication, 115.

Harker (J. A.) On a New Type of Electric Furnace, with a Redetermination of the Melting Point of Platinum, 235.

Hartley (W. N.) The Absorption Spectra and Fluorescence of Mercury Vapour, 428.

Heat, method of finding conductivity for (Niven), 34.

- Heats, specific and latent, studied with liquid hydrogen and air calorimeters (Dewar), 325.
- Helium in air, determination of (Ramsay), 111.
- Hopkinson (B.) and Rogers (F.) The Elastic Properties of Steel at High Temperatures, 419.
- Huggins (Sir W.) Presidential address delivered November 30, 1904, 1; — and Lady Huggins. On the Spectrum of the Spontaneous Luminous Radiation of Radium. Part III.—Radiation in Hydrogen, 488.
- Ice, formation of, and structure of glaciers (Quincke), 431.
- Ionic velocities, accurate measurement of (Denison and Steele), 556.
- Ions, transit in electric arc (Swinton), 553.
- Iron carbonyl, physical and chemical properties of (Dewar and Jones), 558.
- Jackson (F. H.) The Basic Gamma-Function and the Elliptic Functions, 127.
- J Jeans (J. H.) On the Application of Statistical Mechanics to the General Dynamics of Matter and Ether, 296; — On the Laws of Radiation, 545.
- Jones (H. O.) See Dewar and Jones.
- Larmor (J.) Note on Dr. S. J. Barnett's paper, 369.
- Light, repulsion of, analogy with Lesage's theory of gravitation (Darwin), 387; — theory of reflection near polarising angle (Maclaurin), 49.
- Lockyer (Sir N.) Further Researches on the Temperature Classification of Stars. No. 2, 145; — On the Observations of Stars made in some British Stone Circles.—Preliminary Note, 177; — and W. J. S. The Flow of the River Thames in Relation to British Pressure and Rainfall Changes, 494.
- Lunt (J.) On the Spectrum of Silicon; with a Note on the Spectrum of Fluorine, 118.
- Lyons (H. G.) On the Relation between Variations of Atmospheric Pressure in North-East Africa and the Nile Flood, 66.
- Maclaurin (R. C.) Theory of the Reflection of Light near the Polarising Angle, 49 — On Newton's Rings formed by Metallic Reflection, 515.
- McLeod (C.) Records of Difference of Temperature between McGill College Observatory and the Top of Mount Royal, Montreal, 415.
- Magnetic declination near Royal Alfred Observatory, Mauritius (Claxton), 507.
- Magnetic disturbance, area of local, in East Loch Roag, Hebrides (Field), 181.
- Magnetic field, electric effect of rotating dielectric in (Barnett), 367; (Larmor), 369.
- Magnetic qualities of iron-free alloys (Fleming and Hadfield), 271.
- Manley (J. J.) See Veley and Manley.
- Mauritius, magnetic declination near Royal Alfred Observatory (Claxton), 507.
- Mees (C. E. K.) See Sheppard and Mees.
- Mercury vapour, absorption spectrum and fluorescence of (Hartley), 428.
- Metal glasses, films, etc., colours in (Garnett), 370.
- Metals, influence of phase changes on tenacity of (Beilby), 462.
- Meteors, Bielid (Downing), 266.
- Micrometer, improved electric (Shaw), 350.
- Milne (J.) Preliminary Notes on Observations made with a Horizontal Pendulum in the Antarctic Regions, 284.
- Morrow (J.) On the Distribution of Velocity in a Viscous Fluid over the Cross-section of a Pipe, and on the Action at the Critical Velocity, 205.

- Neon in air, determination of (Ramsay), 111.
- Newton's rings formed by metallic reflection (Maclaurin), 515.
- Nile flood, relation to atmospheric pressure in North-East Africa (Lyons), 66.
- Niven (C.) On a Method of Finding the Conductivity for Heat, 34.
- Noble (Sir A.) Researches on Explosives.—Part III, 381 ; Supplementary Note, 512.
- Oldham (R. D.) The Rate of Transmission of the Guatemala Earthquake, April 19, 1902, 102.
- Peake (A. H.) The Determination of the Specific Heat of Superheated Steam by Throttling and other Experiments, 185.
- Pendulum, horizontal, observations with in Antarctic Regions (Milne), 284.
- Perman (E. P.) The Direct Synthesis of Ammonia, 167 ; — and Davies (J. H.) Determination of Vapour-pressure by Air-bubbling, 174.
- Petavel (J. E.) The Pressure of Explosions.—Experiments on Solid and Gaseous Explosives, 492.
- Phillips (P.) See Poynting and Phillips.
- Photographic development, chemical dynamics of (Sheppard and Mees), 217 ; — negative, microscopic structure of (Sheppard and Mees), 217.
- Pipes, flow of water in, distribution of velocity and action at critical velocity (Morrow), 205.
- Platinum, melting-point of (Harker), 235.
- Poynting (J. H.) and Phillips (P.) An Experiment with the Balance to find if Change of Temperature has any Effect upon Weight, 445.
- Prideaux (E. B. R.) See Cuthbertson and Prideaux.
- Quincke (G.) The Formation of Ice and the Grained Structure of Glaciers, 431.
- Radiation, laws of (Jeans), 545.
- Radio-active element, new (Hahn), 115 ; — minerals (Strutt), 88, 312.
- Radium, spectrum of radiation of, in hydrogen (Huggins), 488.
- Ramsay (Sir Wm.) A Determination of the Amounts of Neon and Helium in Atmospheric Air, 111.
- Rayleigh (Lord) On the Influence of Collisions, and of the Motion of Molecules in the Line of Sight, upon the Constitution of a Spectrum Line, 440.
- Reflection, metallic, and Newton's rings (Maclaurin), 515.
- Refractive index of gaseous fluorine (Cuthbertson and Prideaux), 426 ; — indices of sulphuric acid (Veley and Manley), 469.
- Rogers (F.) See Hopkinson and Rogers.
- Shaw (P. E.) The Improved Electric Micrometer, 350 ; — The Amplitude of the Minimum Audible Impulsive Sound, 360.
- Sheppard (S. E.) and Mees (C. E. K.) The Theory of Photographic Processes, Part II : On the Chemical Dynamics of Development, including the Microscopy of the Image, 217.
- Silicon, spectrum of (Lunt), 118.
- Simplon tunnel—distribution of temperature encountered (Fox), 29.
- Simpson (G. C.) Atmospheric Electricity in High Latitudes, 160.
- Sound, amplitude of minimum audible impulsive (Shaw), 360.
- Spectra of europium and Sb (Crookes), 411.
- Spectrum line, influence of collisions, etc., upon constitution of (Rayleigh), 440.

- Spectrum of star, evolution of, from nebula (Wilson), 380.
- Stars, temperature classification of (Lockyer), 145 ; evolution of spectra (Wilson), 374.
- Statistical mechanics applied to dynamics of matter and ether (Jeans), 296.
- Steam, specific heat of superheated (Peake), 185.
- Steel, elastic properties at high temperatures (Hopkinson and Rogers), 419.
- Steele (B. D.) See Denison and Steele.
- Stone circles, observations of stars made in (Lockyer), 177.
- Strutt (R. J.) On the Radio-active Minerals, 88 ; — Note Supplementary to a Paper "On the Radio-active Minerals," 312.
- Sulphuric acid, refractive indices (Veley and Manley), 469 ; — electrical conductivity of dilute solutions of (Whetham), 577.
- Swinton (A. A. C.) The Transit of Ions in the Electric Arc, 553.
- Temperature, difference of, between McGill College and Mount Royal, Montreal (McLeod), 415.
- Thames flow in relation to pressure and rainfall changes (Lockyer), 494.
- Thermo-electric junction for determining low temperatures (Dewar), 316.
- Thermo-junctions, study of, at high temperatures (Harker), 235.
- Thorianite, new radio-active element from (Hahn), 115 ; — new mineral from Ceylon (Dunstan and Blake), 253.
- Uranium, connection with radium (Strutt), 88.
- Vapour-pressure, determination by air-bubbling (Perman and Davies), 174.
- Veley (V. H.) and Manley (J. J.) The Refractive Indices of Sulphuric Acid at Different Concentrations, 469.
- Water, flow in pipes (Morrow), 205.
- Weight, relation to change of temperature (Poynting and Phillips), 445.
- Whetham (W. C. D.) The Electrical Conductivity of Dilute Solutions of Sulphuric Acid, 577.
- Wilson (W. E.) The Evolution of the Spectrum of a Star during its Growth from a Nebula, 374.

END OF THE SEVENTY-SIXTH VOLUME (SERIES A).

April 6, 1905.

Sir WILLIAM HUGGINS, K.C.B., O.M., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read:—

- I. "On Reciprocal Innervation of Antagonistic Muscles.—Seventh Note." By Professor C. S. SHERRINGTON, F.R.S.
- II. "The Influence of Cobra-Venom on the Proteid Metabolism." By Dr. JAMES SCOTT. Communicated by Sir THOMAS R. FRASER, F.R.S.
- III. "Further Experiments and Histological Investigations on Intumescences, with some Observations on Nuclear Division in Pathological Tissues." By Miss E. DALE. Communicated by Professor H. MARSHALL WARD, F.R.S.
- IV. "On the Toxin-Antitoxin Reaction, with Special Reference to the Neutralisation of Lysin by Antilysin." By J. A. CRAW. Communicated by Dr. C. J. MARTIN, F.R.S.
- V. "On the Nature of the Silver Reaction in Animal and Vegetable Tissues." By Professor A. B. MACALLUM. Communicated by Professor W. D. HALIBURTON, F.R.S.
- VI. "On Endophytic Adaptation shown by *Erysiphe Graminis* DC. under Cultural Conditions." By E. S. SALMON. Communicated by Professor H. MARSHALL WARD, F.R.S.
- VII. "Ovulation and Degeneration of Ova in the Rabbit." By WALTER HEAPE. Communicated by A. SEDGWICK, F.R.S.

April 13, 1905.

Sir WILLIAM HUGGINS, K.C.B., O.M., President, in the Chair.

Professor J. W. Gregory (elected 1901) was admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "On a New Type of Electric Furnace, with a Re-determination of the Melting-point of Platinum." By Dr. J. A. HARKER.
Communicated by Dr. R. T. GLAZEBROOK, F.R.S.
- II. "On Colour Vision by Very Weak Light." By Dr. G. J. BURCH,
F.R.S.
- III. "The Improved Electric Micrometer." By Dr. P. E. SHAW.
Communicated by Professor J. H. POYNTING, F.R.S.
- IV. "The Amplitude of the Minimum Audible Impulsive Sound."
By Dr. P. E. SHAW. Communicated by Professor J. H.
POYNTING, F.R.S.
- V. "The Refractive Indices of Sulphuric Acid." By Dr. V. H.
VELEY, F.R.S., and J. J. MANLEY.
- VI. "On the Intensity and Direction of the Force of Gravity in
India." By Lieut.-Colonel S. G. BURRARD, F.R.S.
- VII. "A Quantitative Study of Carbon Dioxide Assimilation and
Leaf-temperature in Natural Illumination." By F. F.
BLACKMAN and Miss G. MATTHAEI. Communicated by
FRANCIS DARWIN, For. Sec. R.S.

The Society adjourned over the Easter Recess to Thursday,
May 11.

May 11, 1905.

Annual Meeting for the Election of Fellows.

Sir WILLIAM HUGGINS, K.C.B., O.M., President, in the Chair.

The Statutes relating to the Election of Fellows having been read, Professor Gray and Professor Farmer were, with the consent of the Society, nominated Scrutators, to assist the Secretaries in the examination of the balloting lists.

The votes of the Fellows present were collected, and the following Candidates were declared duly elected into the Society :—

Adami, John George.	Lamplugh, George William.
Bone, William Arthur.	Macbride, Ernest William.
Campbell, John Edward.	Oliver, Francis Wall.
Dines, William Henry.	Prain, David, Lieut.-Col. I.M.S.
Field, Arthur Mostyn, Capt. R.N.	Searle, George F. C.
Forster, Martin Onslow.	Strutt, Hon. Robert John.
Goodrich, Edwin S.	Whittaker, Edmund Taylor.
Hopkins, Frederick Gowland.	

Thanks were given to the Scrutators.

May 11, 1905.

Sir WILLIAM HUGGINS, K.C.B., O.M., President, in the Chair.

Captain F. W. Hutton (elected 1892) was admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

Professor Ludimar Hermann, Professor Henrik Anton Lorentz, Professor Henri Moissan, and Professor Hugo de Vries, were elected Foreign Members of the Society.

The following Papers were read :—

- I. "On the Resemblances existing between the 'Plimmer's Bodies' of Malignant Growths, and certain Normal Constituents of Reproductive Cells of Animals." By Professor J. B. FARMER, F.R.S., J. E. S. MOORE, and C. E. WALKER.
- II. "The Effect of Plant Growth and of Manures upon the Soil: the Rentention of Bases by the Soil." By A. D. HALL and Dr. N. H. J. MILLER. Communicated by Professor H. E. ARMSTRONG, F.R.S.

- III. "A Study of the Process of Nitrification with reference to the Purification of Sewage." By Miss H. CHICK. Communicated by Professor H. MARSHALL WARD, F.R.S.
 - IV. "Pathological Report on the Histology of Sleeping Sickness and Trypanosomiasis; with a Comparison of the Changes found in Animals infected with *T. gambiense* and other Trypanosomata." By Dr. A. BREINL. Communicated by Professor R. BOYCE, F.R.S.
 - V. "The Experimental Treatment of Trypanosomiasis in Animals." By Dr. H. WOLFERSTAN THOMAS. Communicated by Professor R. BOYCE, F.R.S.
 - VI. "Remarks on Mr. Plimmer's Note on the Effects produced in Rats by the Trypanosomata of Gambian Fever and Sleeping Sickness." By Dr. H. WOLFERSTAN THOMAS. Communicated by Professor R. BOYCE, F.R.S.
 - VII. "On the Cytology of Apogamy and Apospory. II.—Preliminary Note on Apospory." By Miss L. DIGBY. Communicated by Professor FARMER, F.R.S.
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May 18, 1905.

Sir WILLIAM HUGGINS, K.C.B., O.M., President, in the Chair.

Mr. John Edward Campbell, Capt. Arthur Mostyn Field, Dr. Martin Onslow Forster, Mr. George F. C. Searle, and the Hon. Robert John Strutt, were admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "On Lesage's Theory of Gravitation and the Repulsion of Light." By Professor G. H. DARWIN, F.R.S.
- II. "The Atomic Weight of Chlorine: an Attempt to Determine the Equivalent of Chlorine by Direct Burning with Hydrogen." By Professor H. B. DIXON, F.R.S., and E. C. EDGAR.
- III. "The Flow of the River Thames in Relation to British Pressure and Rainfall." By Sir NORMAN LOCKYER, K.C.B., F.R.S., and Dr. W. J. S. LOCKYER.
- IV. "Thorianite, a New Mineral from Ceylon." By Professor W. R. DUNSTAN, F.R.S., and G. S. BLAKE.

- V. "A Modified Apparatus for the Measurement of Colour, and its Application to the Determination of the Colour Sensations." By Sir WILLIAM ABNEY, K.C.B., F.R.S.
- VI. "Further Observations on the Germination of the Seed of the Castor Oil Plant (*Ricinus communis*)." By Professor J. REYNOLDS GREEN, F.R.S., and H. JACKSON.
- VII. "On the Efferent Relationship of the Optic Thalamus and Deiter's Nucleus to the Spinal Cord, with Special Reference to the Cerebellar Influx Theory (Hughlings Jackson) and the Genesis of Decerebrate Rigidity (Sherrington)." By Dr. F. H. THIELE. Communicated by Sir VICTOR HORSLEY, F.R.S.
- VIII. "On Reciprocal Innervation of Antagonistic Muscles. Eighth Note." By Professor C. S. SHERRINGTON, F.R.S.
- IX. "The Structure and Function of Nerve Fibres. Preliminary Communication and Addendum." By Professor G. S. MACDONALD. Communicated by Professor C. S. SHERRINGTON, F.R.S.
- X. "On the Occurrence of *Anopheles (Myzomyia) Listoni* in Calcutta." By Major A. ALCOCK, C.I.E., F.R.S., and Major J. R. ADIE.
- XI. "On the Chemical Mechanism of Gastric Secretion." By Dr. J. S. EDKINS. Communicated by Professor C. S. SHERRINGTON, F.R.S.
- XII. "Contributions to the Physiology of Mammalian Reproduction. Part I.—The Œstrous Cycle in the Dog. Part II.—The Ovary as an Organ of Internal Secretion." By F. H. A. MARSHALL and W. A. JOLLY. Communicated by Professor E. A. SCHÄFER, F.R.S.

May 25, 1905.

Sir WILLIAM HUGGINS, K.C.B., O.M., President, in the Chair.

Dr. William Arthur Bone, Mr. William Henry Dines, Dr. Frederick Gowland Hopkins, and Professor Ernest William MacBride, were admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The Croonian Lecture, "On the Globulins," was delivered by Mr. W. B. Hardy, F.R.S.

June 8, 1905.

Sir WILLIAM HUGGINS, K.C.B., O.M., President, in the Chair.

Mr. E. S. Goodrich and Mr. E. T. Whittaker were admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Researches on Explosives. Part III." By Sir ANDREW NOBLE, Bart., K.C.B., F.R.S.
- II. "On the Thermo-Electric Junction as a Means of Determining the Lowest Temperatures." By Sir JAMES DEWAR, F.R.S.
- III. "Studies with the Liquid Hydrogen and Air Calorimeters." By Sir JAMES DEWAR, F.R.S.
- IV. "Colours in Metal Glasses, and in Metallic Films and Metallic Solution." By J. C. MAXWELL GARNETT. Communicated by Professor J. LARMOR, Sec. R.S.
- V. "On the Application of Statistical Mechanics to the General Dynamics of Matter and Ether. The General Method of Statistical Mechanics." By J. H. JEANS. Communicated by Professor J. LARMOR, Sec. R.S.
- VI. "On the Magnetic Qualities of some Alloys not containing Iron." By Professor J. A. FLEMING, F.R.S., and R. A. HADFIELD.
- VII. "On the Phosphorescent Spectra of S8 and Europium." By Sir WILLIAM CROOKES, F.R.S.
- VIII. "On the Perturbations of the Bielid Meteors." By Dr. A. M. W. DOWNING, F.R.S.
- IX. "The Asymptotic Expansion of Integral Functions defined by Taylor's Series." By Rev. E. W. BARNES. Communicated by Professor A. R. FORSYTH, F.R.S.
- X. "Preliminary Note on Observations made with a Horizontal Pendulum in the Antarctic Regions." By Professor J. MILNE, F.R.S.
- XI. "Note supplementary to a Paper 'On the Radio-Active Minerals.'" By Hon. R. J. STRUTT, F.R.S.
- XII. "The Morphology of the Ungulate Placenta, particularly the Development of that Organ in the Sheep, and Notes upon the Placenta of the Elephant and Hyrax." By R. ASSHETON. Communicated by A. SEDGWICK, F.R.S.

- XIII. "A Preliminary Communication on the Life-History of *Trypanosoma balbianii*." By W. S. PERRIN. Communicated by A. SEDGWICK, F.R.S.
- XIV. "On the Effect of Carbon Dioxide on Geotropic Curvature of the Roots of *Pisum Sativum* L." By E. DRABBLE and Miss H. LAKE. Communicated by Professor J. B. FARMER, F.R.S.
- XV. "The Pharmacology of Indaconitine and Bikhacnitine." By Professor J. T. CASH, F.R.S., and Professor W. R. DUNSTAN, F.R.S.
- XVI. "Preliminary Note on the Occurrence of Microsporangia in Organic Connection with the Foliage of *Lyginodendron*." By R. KIDSTON, F.R.S.
- XVII. "Chitin in the Carapace of *Pterygotus Osiliensis* from the Silurian of Oesel." By Dr. OTTO ROSENHEIM. Communicated by Professor W. D. HALLIBURTON, F.R.S.
- XVIII. "The Synthesis of a Substance allied to Adrenalin." By H. D. DAKIN. Communicated by Professor E. H. STARLING, F.R.S.
- XIX. "On the Physiological Activity of Substances indirectly allied to Adrenalin." By H. D. DAKIN. Communicated by Professor E. H. STARLING, F.R.S.
- XX. "On the Refractive Index of Gaseous Fluorine." By C. CUTHBERTSON and E. B. R. PRIDEAUX. Communicated by Sir W. RAMSAY, K.C.B., F.R.S.
- XXI. "The Evolution of the Spectrum of a Star during its Growth from a Nebula." By Dr. W. E. WILSON, F.R.S.
- XXII. "Records of Difference of Temperature between the McGill College Observatory and the Top of Mount Royal, Montreal." By Professor C. MCLEOD. Communicated by Professor CALLENDAR, F.R.S.
- XXIII. "The Elastic Properties of Steel at High Temperatures." By Professor B. HOPKINSON and F. ROGERS. Communicated by Professor EWING, F.R.S.
- XXIV. "On a New Species of *Cephalodiscus* from the Antarctic Ocean." By Professor E. RAY LANKESTER, F.R.S.

The Society adjourned over the Long Vacation to Thursday, November 16.

MINUTES OF MEETINGS.—SESSION 1905-6.

November 16, 1905.

Sir WILLIAM HUGGINS, K.C.B., O.M., President, followed by
Professor CAREY FOSTER, in the Chair.

Mr. George W. Lamplugh, Professor Francis W. Oliver, and
Lieutenant-Colonel David Prain were admitted into the Society.

A List of the Presents received was laid on the table, and thanks
ordered for them.

In pursuance of the Statutes, notice of the ensuing Anniversary
Meeting was given from the Chair.

Dr. Horace Brown, Captain E. W. Creak, and Professor G. M.
Minchin were elected Auditors of the Treasurer's accounts on the part
of the Society.

The following Papers, received during the Recess and published or
in course of publication, in accordance with the Standing Orders of
Council, were read in title :—

“The Absorption Spectrum and Fluorescence of Mercury Vapour.”
By Professor W. N. HARTLEY, F.R.S.

“On the Origin and Life-History of the Interstitial Cells of the Ovary
in the Rabbit.” By Miss J. E. LANE-CLAYTON. Communicated
by Professor E. H. STARLING, F.R.S.

“The Formation of Ice and the Grained Structure of Glaciers.” By
Professor G. QUINCKE, For. Mem. R.S.

“Preliminary Report on a Survey of Magnetic Declination near the
Royal Alfred Observatory, Mauritius.” By T. F. CLAXTON.
Communicated by Dr. C. CHREE, F.R.S.

“Transmission and Inoculability of *Spirillum Theileri* (Laveran).” By
Dr. A. THEILER. Communicated by Colonel BRUCE, C.B., F.R.S.

“Note on the Mechanism of the Ascent of Sap in Trees.” By
Professor J. LARMOR, Sec. R.S.

“On the Influence of Collisions and of the Motion of Molecules in the
Line of Sight upon the Constitution of a Spectrum Line.” By
Lord RAYLEIGH, O.M., F.R.S.

“An Experimental Enquiry into the Nature of the Substance in Serum
which influences Phagocytosis.” By Dr. G. DEAN. Communicated
by Professor J. R. BRADFORD, F.R.S.

- "An Experiment with the Balance to find if Change of Temperature has any Effect upon Weight." By Professor J. H. POYNTING, F.R.S., and P. PHILLIPS.
- "The Phagocytosis of Red Blood-Cells." By Dr. J. O. WAKELIN BARRATT. Communicated by Sir V. HORSLEY, F.R.S.
- "A New Formation of Diamond." By Sir W. CROOKES, F.R.S.
- "The Influence of Phase Changes on the Tenacity of Ductile Metals at the Ordinary Temperature and the Boiling Point of Liquid Air." By G. T. BEILBY and H. N. BEILBY. Communicated by Professor J. LARMOR, Sec. R.S.
- "On the Probable Existence of Emulsin in Yeast." By Dr. T. A. HENRY and Dr. S. J. M. AULD. Communicated by Professor W. R. DUNSTAN, F.R.S.
- "A Preliminary Note on the Susceptibility of Goats to Malta Fever." By Dr. T. ZAMMIT. Communicated by Colonel BRUCE, C.B., F.R.S.
- "Preliminary Note on Goats as a Means of Propagation of Mediterranean Fever." By Major W. H. HORROCKS. Communicated by Colonel BRUCE, C.B., F.R.S.
- "Studies on Enzyme Action. VII.—The Synthetic Action of Acids contrasted with that of Enzymes. Synthesis of Maltose and Isomaltose. VIII.—The Mechanism of Fermentation." By Dr. E. F. ARMSTRONG. Communicated by Professor H. E. ARMSTRONG, F.R.S.
- "Studies on Enzyme Action.—Lipase." By Professor H. E. ARMSTRONG, F.R.S.
- "Inheritance of Heterostylism in *Primula*." By W. BATESON, F.R.S., and R. P. GREGORY.
- "Fertility in Scottish Sheep." By Dr. F. H. A. MARSHALL. Communicated by Professor SCHÄFER, F.R.S.
- "On the Spectrum of the Spontaneous Luminous Radiation of Radium. Part III.—Radiation in Hydrogen." By Sir W. HUGGINS, K.C.B., Pres. R.S., and Lady HUGGINS.
- "Researches on Explosives.—Part III. Supplementary Note." By Sir ANDREW NOBLE, Bart., F.R.S.
- "Report on the Anatomy of the Tsetse Fly (*Glossina palpalis*)." By Professor E. A. MINCHIN. Communicated by Professor RAY LANKESTER, F.R.S.
- "On the Isolation of the Infecting Organism (*Zoochlorella*) of *Convoluta Roscoffensis*." By F. KEEBLE and F. W. GAMBLE. Communicated by Professor S. J. HICKSON, F.R.S.

The following Papers were read :—

- I. "The Physical and Chemical Properties of Iron Carbonyl." By Sir JAMES DEWAR, F.R.S., and H. O. JONES.
- II. "The Transit of Ions in the Electric Arc." By A. A. CAMPBELL SWINTON. Communicated by the Hon. C. A. PARSONS, C.B., F.R.S.
- III. "First Photographs of the Canals of Mars." By Professor PERCIVAL LOWELL. Communicated by Sir J. NORMAN LOCKYER, K.C.B., F.R.S.
- IV. "On the Laws of Radiation." By Professor J. H. JEANS. Communicated by Professor J. LARMOR, Sec. R.S.
- V. "The Pressure of Explosions. Experiments on Solid and Gaseous Explosives." By J. E. PETAVEL. Communicated by Professor A. SCHUSTER, F.R.S.
- VI. "The Accurate Measurement of Ionic Velocities." By Dr. R. B. DENISON and Dr. B. D. STEELE. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.
- VII. "On Newton's Rings formed by Metallic Reflection." By Professor R. C. MACLAURIN. Communicated by Professor J. LARMOR, Sec. R.S.
- VIII. "The Electrical Conductivity of Dilute Solutions of Sulphuric Acid." By W. C. D. WHETHAM, F.R.S.

November 23, 1905.

Sir W. D. NIVEN, Vice-President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair, and the list of the Officers and Council for the ensuing year proposed by the Council for election was read as follows :—

President.—The Lord Rayleigh, O.M., M.A., D.C.L.

Treasurer.—Alfred Bray Kempe, M.A.

Secretaries.—{ Professor Joseph Larmor, D.Sc., D.C.L., LL.D.
 { Sir Archibald Geikie, D.C.L., Sc.D., LL.D.

Foreign Secretary.—Francis Darwin, M.A., M.B.

Other Members of the Council.—Shelford Bidwell, Sc.D. ; Sir T. Lauder Brunton, M.D. ; Professor J. Norman Collie, Ph.D. ; Professor Wyndham R. Dunstan, M.A. ; Professor John Bretland Farmer,

M.A.; Professor Francis Gotch, D.Sc.; Sidney Frederic Harmer, Sc.D.; Sir William Huggins, K.C.B., O.M.; Professor Edwin Ray Lankester, M.A.; John Edward Marr, Sc.D.; George Ballard Mathews, M.A.; Hugh Frank Newall, M.A.; Sir William Davidson Niven, K.C.B.; Professor John Perry, D.Sc.; Professor Ernest Henry Starling, M.D.; Professor William Augustus Tilden, D.Sc.

The following Papers were read :—

- I. "On the Nature of the Galvanotropic Irritability of Roots." By Dr. A. J. EWART and Miss BAYLISS. Communicated by FRANCIS DARWIN, For. Sec. R.S.
- II. "Some Observations on *Welwitschia mirabilis*, Hooker-f." By Professor H. H. W. PEARSON. Communicated by A. C. SEWARD, F.R.S.
- III. "On the Effects of Alkalies and Acids, and of Alkaline and Acid Salts, upon Growth and Cell Division in the Fertilised Eggs of *Echinus esculentus*. A Study in Relationship to the Causation of Malignant Disease." By Professor B. MOORE, Dr. H. E. ROAF, and E. WHITLEY. Communicated by Professor W. A. HERDMAN, F.R.S.
- IV. "A Note on the Effect of Acid, Alkali, and certain Indicators in Arresting or otherwise Influencing the Development of the Eggs of *Pleurocetes platessa* and *Echinus esculentus*." By E. WHITLEY. Communicated by Professor W. A. HERDMAN, F.R.S.
- V. "On Certain Physical and Chemical Properties of Solutions of Chloroform and other Anæsthetics. A Contribution to the Chemistry of Anæsthesia. (Second Communication.)" By Professor B. MOORE and Dr. H. E. ROAF. Communicated by Professor SHERRINGTON, F.R.S.
- VI. "On the Possibility of Determining the Presence or Absence of Tubercular Infection by the Examination of a Patient's Blood or Tissue Fluids." By Dr. A. E. WRIGHT and Staff-Surgeon S. T. REID, R.N. Communicated by Sir J. BURDON SANDERSON, Bart., F.R.S.
- VII. "On Spontaneous Phagocytosis and on the Phagocytosis which is obtained with the Heated Serum of Patients who have responded to Tubercular Infection, or, as the case may be, to the Inoculation of a Tubercle Vaccine." By Dr. A. E. WRIGHT and Staff-Surgeon S. T. REID, R.N. Communicated by Sir J. BURDON SANDERSON, Bart., F.R.S.
- VIII. "On the Occurrence of Heterotypical Mitoses in Cancer." By Dr. E. F. BASHFORD and J. A. MURRAY. Communicated by Professor J. ROSE BRADFORD, F.R.S.

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